

CRANFIELD UNIVERSITY

Andrew Joseph Hargreaves

**Developing a Treatment Technology for the Removal of
Trace Metals from Municipal Wastewater**

Cranfield Water Science Institute
School of Water, Energy and Environment

PhD

Academic Year: 2014 – 2017

Academic Supervisors:

Dr. Pablo Campo Moreno and Dr. Gabriela Dotro

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ABSTRACT

The implementation of bioavailability-based water quality standards for metals in the United Kingdom, Europe and the United States is likely to challenge water utilities to reduce the concentrations of metals in effluent discharges. Municipal wastewater treatment works (WWTWs) are not, however, specifically designed to remove metals, with current treatment technologies providing a relatively low and inconsistent level of removal. New technologies will therefore be required to achieve removal rates to meet potentially more stringent discharge criteria. Improvements in the understanding of the form of metals in effluent is crucial for the development of technologies to reduce metal concentrations in effluent discharges.

In the present study, effluent samples were separated into three parts; a particulate fraction ($> 0.45 \mu\text{m}$), a 'colloidal' fraction ($0.45 \mu\text{m} - 1 \text{ kDa}$) and a 'truly dissolved' ($< 1 \text{ kDa}$) size fraction. Soluble (i.e. $< 0.45 \mu\text{m}$) copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) was found to be distributed predominantly in the colloidal fraction, and therefore technologies capable of removing particles from the colloidal fraction have good potential to reduce the concentration of these metals in effluent.

Bench-scale studies tested the coagulation-flocculation (CF) treatment process and found this treatment approach to be effective for the removal of Cu, Pb and Zn from effluent, but was not effective at removing Ni. Two different CF treatment technologies were assessed, namely, the biopolymer, Flocculan, and a conventional coagulant, ferric chloride (FeCl_3). Flocculan and FeCl_3 demonstrated similar removal rates for metals (except for Cu, for which Flocculan offered a better level of removal), however, Flocculan maintained the concentration of dissolved organic carbon (DOC), which offers an important control on metal bioavailability. Flocculan therefore simultaneously reduces metal concentrations and bioavailability whereas FeCl_3 reduces metal concentrations and DOC in proportion and therefore bioavailability is unaffected. Flocculan offers the opportunity to control the concentrations of trace metals in effluent in an environmentally and financially sustainable manner.

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ABBREVIATIONS

AA	Annual Average
ABC	Ambient Background Concentration
AC	Activated Carbon
APHA	American Public Health Association
ANZECC	Australian and New Zealand Environment and Conservation Council
ARMCANZ	Agriculture and Resource Management Council of Australia and New Zealand
AS	Activated Sludge
BDL	Below Detection Limit
BLM	Biotic Ligand Model
BNR	Biological Nutrient Removal
BOD	Biochemical Oxygen Demand
CAPEX	Capital Expenditure
CCC	Criteria Continuous Concentration
CF	Coagulation-flocculation
CI	Confidence Interval
CIP	Chemicals Investigation Programme
CMC	Criteria Maximum Concentration
COC	Colloidal Organic Carbon
COD	Chemical Oxygen Demand
CoV	Coefficient of Variation
CW	Constructed Wetland
DOC	Dissolved Organic Carbon
EC	European Commission
EDTA	Ethylenediaminetetraacetic Acid
EPS	Extra-cellular Polymeric Substances
EQS	Environmental Quality Standard
FSC	Forest Stewardship Council
FTIR	Fourier Transform Infrared Spectroscopy
GAC	Granular Activated Carbon
GEH	Granulated Ferric Hydroxide

HF	Horizontal Subsurface Flow
HMM	High Molar Mass
HRT	Hydraulic Retention Time
HS	Humic Substance
HT	Holding Tank
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
KT	Kepner Tregoe
LMM	Low Molar Mass
MAC	Maximum Allowable Concentration
M-BAT	Metal Bioavailability Assessment Tool
MBR	Membrane Bioreactor
MF	Microfiltration
MW	Molecular Weight
MWCO	Molecular Weight Cut Off
NF	Nanofiltration
NSAF	Nitrifying Submerged Aerated Filter
NTA	Nitrilotriacetic acid
OPEX	Operating Expenditure
PAC	Polyaluminium Chloride
PEI	Polyethyleneimine
PHS	Priority Hazardous Substance
RAS	Returned Activated Sludge
RBMP	River Basin Management Plan
RO	Reverse Osmosis
SAS	Surplus Activated Sludge
SD	Standard Deviation
SEM	Scanning Electron Microscopy
SRT	Sludge Retention Time
SUVA	Specific Ultraviolet Absorbance
TF	Trickling Filter
TMP	Transmembrane Pressure
TP	Total Phosphorous
TSS	Total Suspended Solids

UF	Ultrafiltration
UK	United Kingdom
UKTAG	United Kingdom Technical Advisory Group
UNEP	United Nations Environment Programme
US	United States
USEPA	United States Environmental Protection Agency
WFD	Water Framework Directive
WHO	World Health Organisation
WQC	Water Quality Criteria
WWF	World Wide Fund for Nature
WWTWs	Wastewater Treatment Works

All abbreviations are introduced within the text at first use in each individual chapter.

NOTATIONS

Al	Aluminium
Ar	Arsenic
Cd	Cadmium
Ca	Calcium
Cu	Copper
Fe	Iron
FeCl ₃	Ferric Chloride
HCl	Hydrochloric Acid
Hg	Mercury
HgS	Mercury Sulphide
HNO ₃	Nitric Acid
H ₃ O ⁺	Hydronium Ion
H ₃ PO ₄	Phosphoric Acid
K _d	Partition Coefficient
Mg	Magnesium
NaOH	Sodium Hydroxide
NH ₄	Ammonical Nitrogen
Ni	Nickel
Pb	Lead
PO ₄	Phosphate
Sb	Antimony
Zn	Zinc

All notations are introduced within the text at first use in each individual chapter.

Chapter 1

Introduction

1. Introduction

1.1 Background to the project

Discharges from municipal wastewater treatment works (WWTWs) may be a significant source of environmental pollution and pose risks to the aquatic environment (Chambers et al. 1997). Trace metals such as copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) are of particular concern as they are potentially toxic, do not degrade, and are released continuously into the aquatic environment (Gardner et al. 2013). Consequently, there are strong regulatory drivers in place to control releases into the environment. For example, the Water Framework Directive (WFD, 2000/60/EC) classifies Pb and Ni as Priority Substances (Annex X) and Cu and Zn as Specific Pollutants (Annex VIII), and requires that concentrations of these metals are below specified Environmental Quality Standards (EQS). The Environment Agency, the environmental regulator for England, has recently developed a framework for the implementation of bioavailability-based water quality standards for these metals. This regulatory regime takes account of the influence of site-specific physico-chemical conditions such as pH, water hardness and the concentration of dissolved organic carbon (DOC), and utilises computational models based on the biotic ligand model (BLM) to assess risk and to estimate the bioavailable metal fraction (Di Toro et al. 2001). In the United States (US), the use of a BLM to determine Water Quality Criteria for Cu has already been authorised by the US Environmental Protection Agency (USEPA, 2007).

Bioavailability-based standards are expected to reduce acceptable metal concentrations in some instances, the prospect of which has caused concern for WWTWs operators, in particular, because metal removal within existing treatment processes is inconsistent (Ziolko et al. 2011; Gardner et al. 2013). Therefore, to achieve metal removal rates to comply with more stringent discharge quality requirements, the development of novel wastewater treatment technologies is required.

A focus of this study is the form of metals within wastewater and the significance that metal form is thought to play in controlling the extent to which metals are removed. Traditionally metals are considered to exist in two size fractions; a soluble fraction that passes through a filter with a pore size of 0.45 μm , and a particulate fraction which is

retained on the filter (i.e. $> 0.45 \mu\text{m}$). Metals such as Cu and Pb are known to have a high affinity for the particulate fraction and can, therefore, be removed within the wastewater treatment process by means of physical separation (Choubert et al. 2011). In contrast, Ni and Zn dominate in the soluble fraction, which is typically comprised of complexed metal, free metal ions, and metal entrained within colloidal suspensions (Worms et al. 2010; Schijf and Zoll, 2011). In this case, metal removal typically involves expensive and energy intensive adsorption, ion exchange or chemical modification processes (Martin et al. 1995).

Materials within the soluble fraction can be separated into two further size fractions namely, a colloidal fraction, which is composed of material found in the size range 1 kDa to $0.45 \mu\text{m}$, and a truly dissolved fraction containing constituents with a molecular weight lower than 1 kDa (Worms et al. 2010). Metal distribution within the soluble fraction is influenced by the presence of functional groups (ligands) that may complex metal ions. Hence, the quantity and type of organic matter, typically quantified as DOC, exerts an important influence on metal form (Di Toro et al. 2001; Ma et al. 2001). For example, the colloidal size fraction contains macromolecules such as polysaccharides and proteins (Jarusutthirak et al. 2002; Nam and Amy, 2008) to which metals may adsorb to or complex with in wastewater (Pernet-coudrier et al. 2008; Sheng et al. 2013). However, DOC is seldom measured in WWTWs and the role of DOC in the behaviour of metals within effluent is not entirely well understood and thought to be different from that of DOC derived from so-called natural sources (Katsoyiannis and Samara, 2007; Worms et al. 2010; Constantino et al. 2017).

The presence of colloidal material within wastewater may challenge the traditional understanding about how metals behave in solution, in particular, that there are mechanisms other than complexation that influence metal form. Studies on the distribution of metals in WWTWs remain limited to conventional classification (i.e. soluble and particulate) and this simplified characterisation has hindered the understanding of mechanisms influencing metal fractionation in wastewater. This is of particular importance as the removal of both soluble and particulate metal fractions during wastewater treatment may be necessary in order to comply with more stringent discharge quality requirements (Ziolko et al. 2011).

In addition to Cu, Pb, Ni and Zn influent received at WWTWs may also contain mercury (Hg) and antimony (Sb); metals which are not monitored on a regular basis (Choubert et al. 2011) but also have regulatory drivers that require their removal. Hg is classified as a Priority Substance under the WFD (Annex X) which requires that Hg concentrations do not exceed 0.05 µg/L as an annual average and 0.07 µg/L as a maximum allowable concentration. In the United Kingdom (UK), the concentration of Sb in drinking water may not exceed 5 µg/L (Department for Environment, Food and Rural Affairs [DEFRA], 2015) and therefore a combination of low effluent dilution capacity and the siting of drinking water abstraction locations downstream of WWTWs discharges, mean WWTWs operators often seek to reduce the concentration of Sb in effluent. Fundamental knowledge about the fate of Hg and Sb within WWTWs is, however, limited, with relatively few recorded studies investigating their fate and behaviour within the wastewater treatment process (Rogers, 1996; Choubert et al. 2011). This is of particular concern for Severn Trent Water, as elevated concentrations of these metals have been recorded in discharges from one of their treatment works.

1.2 Aims and objectives

The overall aim of this work is to examine the form of Cu, Pb, Ni and Zn within various stages of the municipal wastewater treatment process in order to identify and develop technologies which could be used to improve their removal. The primary objectives are:

1. Review the current knowledge on the fate and removal of metals during conventional wastewater treatment processes and the effectiveness of existing advanced treatment technologies.
2. Evaluate the distribution of Cu, Pb, Ni and Zn in particle size fractions of wastewater.
3. Evaluate the impact of the coagulation-flocculation treatment process on metal form (i.e. particulate, colloidal, and truly dissolved fractions), bioavailability, and removal.

A secondary objective, of specific interest to Severn Trent Water, was to develop an improved understanding of the factors that influence the fate and removal of Hg and Sb

throughout the wastewater treatment process at a specific WWTWs, and examine the technology options available to improve removal.

1.3 Thesis structure

An overview of the content of each of the thesis chapters is given below, with the connection between chapters shown in Figure 1.1. Note that chapters 2, 3, 4, 5 and 7 are in journal article format and have been published. The relevant references are provided at the end of each chapter.

Chapter 1 describes the background and the need for the research that has been undertaken, the research aims and objectives and the thesis structure.

Chapter 2 presents a review of literature on the occurrence of trace metals in municipal wastewater and the behaviour and removal of metals during conventional wastewater treatment processes. The performance of advanced treatments capable of removing metals from municipal wastewater under real world conditions is also evaluated. (Chapter 2, published in *Environmental Technology Reviews* 7 (2018) – *Andrew J. Hargreaves, Carlos Constantino, Gabriela Dotro, Elise Cartmell, Pablo Campo. Fate and removal of metals in municipal wastewater treatment: a review*).

Chapter 3 describes the fractionation of trace metals (Cu, Pb, Ni and Zn) in effluent from a treatment works operating the trickling filter treatment technology. This study was undertaken in order to better understand the potential options to remove metals from municipal wastewater (Chapter 3, published in *Chemosphere* 175 (2017) - *Andrew J. Hargreaves, Peter Vale, Jonathan Whelan, Carlos Constantino, Gabriela Dotro, Elise Cartmell, Pablo Campo. Distribution of trace metals (Cu, Pb, Ni, Zn) between particulate, colloidal and truly dissolved fractions in wastewater treatment*).

Chapter 4 presents a comparison of the effectiveness of a number of coagulation-flocculation (CF) treatment technologies for removing metals from wastewater. The technologies compared were the metal salt ferric chloride (FeCl_3), the synthetic polymer polyethyleneimine, and the biopolymers chitosan and Flocculan (Chapter 4, published in *Clean Technologies and Environmental Policy* 20(2) (2018) - *Andrew J. Hargreaves, Peter Vale, Jonathan Whelan, Luca Alibardi, Carlos Constantino, Gabriela Dotro,*

Elise Cartmell, Pablo Campo. Coagulation-flocculation process with metal salts, synthetic polymers and biopolymers for the removal of trace metals (Cu, Pb, Ni, Zn) from municipal wastewater).

Chapter 5 describes the results of an investigation into the effect of FeCl_3 and Flocculan on metal form (i.e. particulate, colloidal and truly dissolved fractions) and bioavailability in municipal wastewater (Chapter 5, published in *Water Research* 128 (2018) - *Andrew J. Hargreaves, Peter Vale, Jonathan Whelan, Luca Alibardi, Carlos Constantino, Gabriela Dotro, Elise Cartmell, Pablo Campo. Impacts of coagulation-flocculation treatment on the size distribution and bioavailability of trace metals (Cu, Pb, Ni, Zn) in municipal wastewater).*

Chapter 6 presents a discussion on the overall suitability of Flocculan as a treatment technology and the implications of the colloidal fraction for metal bioavailability and the BLM approach. Recommendations for further research are also presented in this chapter.

Chapter 7 describes the results from a study into the fate of Hg and Sb within the wastewater treatment process, and evaluates the treatment options available to enhance Hg and Sb removal (Chapter 7, published in *Water, Air, & Soil Pollution* 227(3) (2016) pages 1-17 – *Andrew J. Hargreaves, Peter Vale, Jonathan Whelan, Carlos Constantino, Gabriela Dotro, Elise Cartmell. Mercury and antimony in wastewater: fate and treatment).* This study was undertaken on behalf of Severn Trent Water in response to a specific concern about elevated concentrations of these metals in discharges from a treatment works.

Chapter 8 summarises the key conclusions of this research in relation to the original objectives.

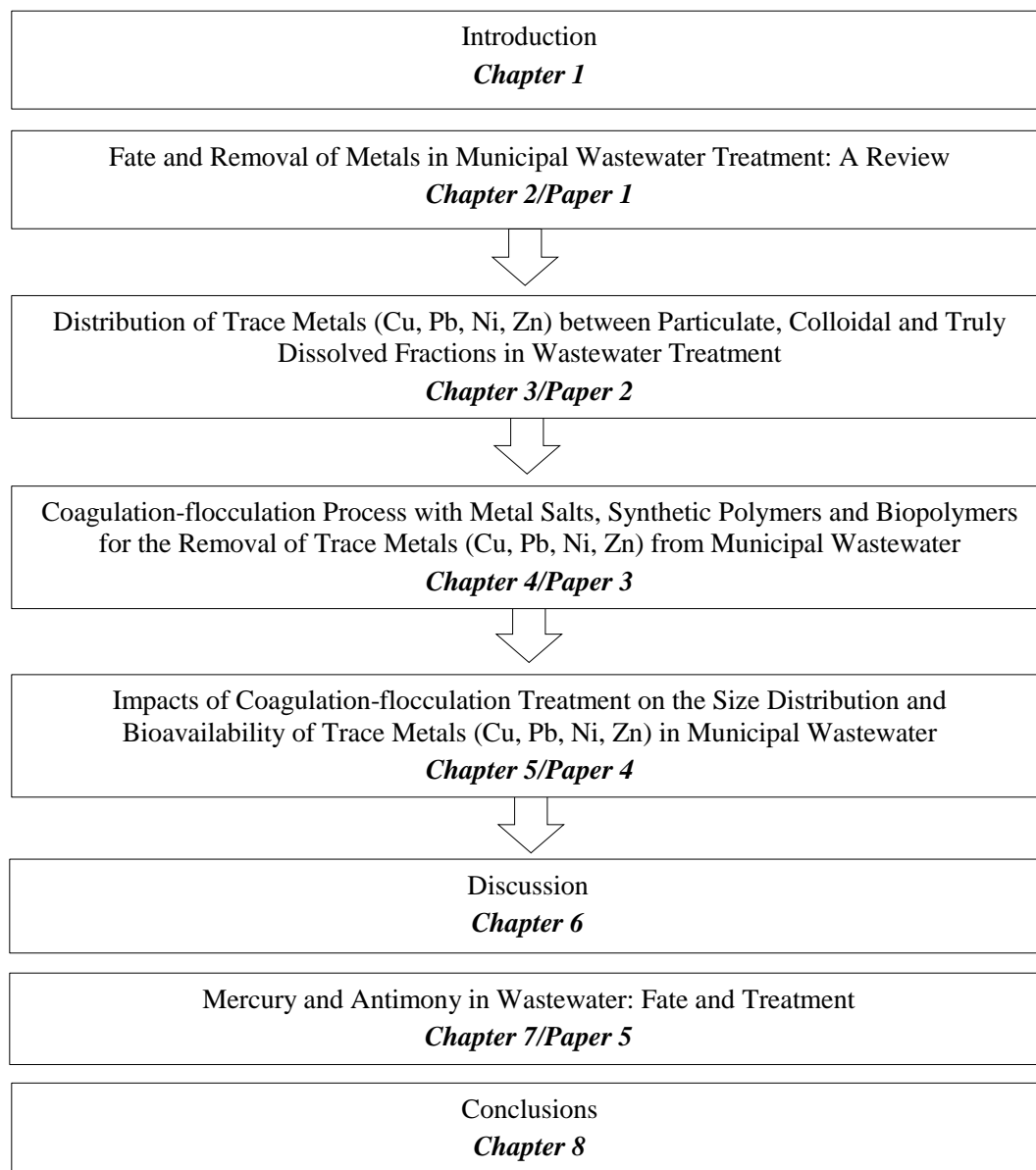


Figure 1.1 Thesis structure as a flow chart.

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Chapter 2

Fate and Removal of Metals in Municipal Wastewater Treatment: A Review

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2. Fate and Removal of Metals in Municipal Wastewater Treatment: A Review

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Abstract

Municipal effluents contain heavy metals in particular copper, lead, nickel and zinc. The concern regarding the impact of these contaminants in the aquatic environment is reflected in the latest criteria revisions to water-related legislation, such as the Clean Water Act in the United States and the Water Framework Directive in Europe. These revisions may lower metal concentrations considered acceptable in final effluents. The study of metal behaviour within the wastewater treatment process is crucial to develop and optimise systems to achieve acceptable metal concentrations in effluent discharges. To comply with more stringent environmental quality standards, utilities may require the implementation of additional treatment technologies. This review evaluates the performance of conventional municipal wastewater treatment processes, that is, primary sedimentation and biological treatment via the activated sludge and trickling filter processes. The mechanisms and parameters affecting metal removal are discussed to evaluate how an understanding of metal behaviour within wastewater treatment processes may allow optimisation and enhancement of conventional treatment processes, or inform the selection of new technologies to enhance trace metal removal. The performance of advanced treatment technologies capable of removing metals from municipal wastewater under real world conditions has also been evaluated.

2.1 Introduction

Municipal effluents pose a significant risk to the aquatic environment and are an important source of environmental pollution (Chambers et al. 1997). Effluents from municipal wastewater treatment works (WWTWs) originate from runoff, industrial and domestic sources, and are known to contain numerous pollutants (Gagnon and Saulnier, 2003). Among them, the metals copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) are classified as potentially toxic elements and may cause problems such as acute or chronic health effects, phytotoxicity and bioaccumulation (Zheng et al. 2007; Alhadrami et al. 2016; Darko et al. 2016). Metals, therefore, potentially pose major environmental and health problems to society (Mudho and Kumar, 2013).

As a consequence of their potential to cause harm, there are regulatory drivers that require Cu, Pb, Ni and Zn to be removed during the wastewater treatment process. The Water Framework Directive (WFD; 2000/60/EC), which classifies Pb and Ni as Priority Substances (Annex X) and Cu and Zn as Specific Pollutants (Annex VIII), requires ‘good’ chemical status to be achieved. Such status is achieved when substance concentrations are lower than specified threshold values (the Environmental Quality Standard, or EQS) expressed either as an Annual Average (AA) or Maximum Acceptable Concentration (MAC). In the United States (US), the Clean Water Act (1972) includes Criterion Continuous Concentration (CCC) and Criterion Maximum Concentration (CMC) standards for heavy metals, to protect aquatic life and human health.

Within the European Union the WFD has specified bioavailability based standards for Pb and Ni, whilst the Environment Agency, the environmental regulator for England, has specified water quality standards for Cu and Zn as permissible bioavailable concentrations. This regulatory regime accounts for site-specific physico-chemical conditions and using computational models, based on the biotic ligand model (BLM), allows the bioavailable metal fraction to be estimated (Di Toro et al. 2001; Peters et al. 2011). Bioavailability-based standards are expected to significantly reduce acceptable metal concentrations at a range of locations in the United Kingdom (Peters et al. 2009). A prospect which has raised concern, as studies have shown that removal rates for Cu, Pb, Ni and Zn vary considerably at WWTWs (Gardner et al. 2013) which may,

therefore, require the optimisation of conventional treatments or the implementation of advanced treatment technologies.

Owing to the prospect of more stringent legislation, a large number of studies investigating the application of advanced treatment technologies for the removal of heavy metal ions from wastewater have been conducted. Technologies include chemical precipitation, membrane filtration, adsorption and ion-exchange, as well as biological treatments such as constructed wetlands (CWs) and membrane bioreactors (MBRs). Many studies have investigated the performance of treatment technologies for the removal of metals from industrial or synthetic wastewater with initial metal concentrations in the mg/L range. It is, however, well-known that the initial metal concentration strongly influences the removal performance of treatment technologies (Saeed et al. 2005; Lim and Aris, 2014; Kumari and Tripathi, 2015), and relatively more metal can be removed from more concentrated influents (Ho and McKay, 2000; Chipasa, 2003; Meena et al. 2008; Üstün, 2009). Given that in municipal effluents metal concentrations are typically in the $\mu\text{g/L}$ range, these studies are of limited applicability to municipal wastewater treatment. There has, however, been no attempt made to review studies in the literature that have investigated the effectiveness of metal removal technologies under real world municipal wastewater conditions (i.e. metal concentrations $\leq 1 \text{ mg/L}$). This gap in knowledge may, therefore, hinder the design and application of suitable treatment technologies to enhance trace metal removal at municipal WWTWs.

A large body of previous work indicates the relevance of understanding metal fate throughout wastewater treatment for the selection and development of suitable techniques to enhance metal removal (Lester 1983; Shafer et al. 1998; Chipasa 2003; Karvelas et al. 2003; Santos and Judd, 2010). For example, metals can be considered to exist in two size fractions; a particulate fraction which is retained separation of metal concentrations into particulate ($> 0.45 \mu\text{m}$) and soluble ($< 0.45 \mu\text{m}$) fractions has determined that metals with a high affinity for particulate matter such as Cu and Pb, can be removed via physical separation (Choubert et al. 2011). Conversely, metals such as Ni and Zn predominate in the soluble fraction which requires adsorption, ion exchange or chemical modification for effective removal (Martin et al. 1995). There is, however,

a need to develop an in-depth understanding of the mechanisms controlling metal fractionation in treated effluent, as the removal of both soluble and particulate metal fractions during wastewater treatment will be necessary in order to comply with more stringent discharge quality requirements (Ziolko et al. 2011).

In this review, the occurrence of trace metals (Cu, Pb, Ni, Zn) in municipal wastewater and the potential of conventional treatment technologies to remove metals from municipal wastewater were critically evaluated. The mechanisms and parameters influencing metals during conventional wastewater treatment were assessed to elucidate how an understanding of metal behaviour may allow optimisation and enhancement of conventional treatment processes, or inform the selection of suitable technologies to enhance trace metal removal at WWTWs. The performance of advanced treatment technologies capable of removing metals from municipal wastewater at environmentally realistic metal concentrations (≤ 1 mg/L), have also been reviewed.

2.2 Water-related legislation

It is accepted that the bioavailability (and subsequently toxicity) of certain metals depends on physico-chemical characteristics, including total suspended solids (TSS), pH, hardness and dissolved organic carbon (DOC). As such, bioavailability-based EQSs have recently been developed for Cu, Pb, Ni and Zn. In the United Kingdom (UK), bioavailability-based standards will be used to assess compliance with EQSs in the second cycle of River Basin Management Plans (RBMP 2, 2015–2020). Prior to the introduction of bioavailability-based standards, in the first round of RBMPs (RBMP 1, 2010–2015), hardness based standards were in use for Cu and Zn, whereby higher metal concentrations were permissible in harder waters.

For RBMP 2 standards, the bioavailable metal concentration is calculated using a BLM. Standards for RBMP 1 and RBMP 2 for Cu, Pb, Ni and Zn are shown in Table 2.1. A notable characteristic of bioavailability-based standards is that the EQS for Zn requires the Ambient Background Concentration (ABC) to be accounted for as part of the assessment of compliance. Zn is widely found at relatively high concentrations compared with other metals, thus, accounting for its ABC helps avoid the setting of regulatory standards which are below ambient background concentrations to which

organisms may be adapted. The metal bioavailability assessment tool (M-BAT) estimates the bioavailable concentration of a metal under the conditions found at a site, and this can be compared with the EQS to assess compliance (WFD-UK Technical Advisory Group [UKTAG], 2014). As of 2007, standards for Cu have been determined using a BLM in the US (USEPA, 2007). Hardness-dependent standards are currently in place for Pb, Ni and Zn in the US (Table 2.1).

Table 2.1 Freshwater EQSs (EU) and WQC (US).

Metal	RBMP 1 (annual average, µg/L)	RBMP 2 (annual average, µg/L)	CCC (µg/L)
Cu	1-28 ^a	1	0.18-20
Pb	7.2	1.2	0.01-7 ^a
Ni	20	4	1-115 ^a
Zn	8-125 ^a	10.9 + ABC	2.4-260 ^a

^a Hardness related values

2.3 Metal sources in wastewater

Industrial emissions have been strongly linked as a source of heavy metals in wastewater as they are used within industrial activities (Jones et al. 2017). In recent years, reduction in the levels of such activity and the application of pre-treatments and clean technologies in the treatment of industrial effluents, has meant that the amount of metals emitted by industrial sources have been declining in many countries (Cantinho et al. 2016). For example, at Rya WWTWs (Sweden), Mattsson et al. (2012) observed a significant reduction in influent metal concentrations due to the sizeable reduction in industrial emissions. In addition, Rule et al. (2006), who analysed influent received at 30 WWTWs in England, reported no correlation between metal concentrations and industrial input. Therefore, the relevance of other metal sources has duly increased due to the consumption and usage of various metal containing goods (Olofsson et al. 2013). According to the European Commission (EC, 2001), an assessment of data collected on metals entering urban wastewater systems in three countries (UK, Norway and France) indicated that domestic inputs were the largest sources of Cu, Pb and Zn. A significant amount of Cu in wastewater comes from drinking water, and elevated metal concentrations in tap water can be attributed to the corrosion of domestic plumbing systems (Merkel et al. 2002; Tamasi and Cini, 2004). Nevertheless, there is evidence

that inputs from plumbing are in decline as a result of phosphate dosing of potable water, which reduces the amount of Cu leaching from plumbing into the water supply (Goh et al. 2008). Drinking water and household stainless steel products are also recognised as an important source of Ni (Ziolko et al. 2011). Despite Pb being banned as a fuel additive, runoff is still a contributing source of this metal in wastewater as a result of its use in old paints, car wheel balancing weights (banned in European Union since 2005) and as a roofing material (Kayhanian, 2012). The main sources of Zn have been found to include personal care products including shampoo and toothpaste, and household agents such as laundry detergent (Sörme and Lagerkvist, 2002; Tsuji-Naito et al. 2007). Additionally, Zn and Cu are also ubiquitous in urban runoff with car tyres, car brake linings and roofing being the respective sources (Councell et al. 2004; Hulskotte et al. 2007).

2.4 Metal concentrations in influent

Heavy metals including Cu, Pb, Ni and Zn are nearly always detectable at WWTWs. Metal concentrations measured worldwide in raw wastewaters are presented in Table 2.2. In general, the lowest concentrations of metals were found for Pb, whilst the metal with the highest values was Zn. However, as shown in the table, influent metal concentrations present highly variable concentrations even within the same country. Such variability is typically attributed to the diverse nature of metal inputs to the sewer system and the location of WWTWs (Wilkie et al. 1996; da Silva Oliveira et al. 2007). In addition, combined sewers and separate sewers are impacted by varying amounts of runoff and therefore metals. In Italy five sites with varying degrees of industrial input were monitored by Carletti et al. (2008) who found notable differences for metals even between sites without industrial contribution (Table 2.2). Temporal variations in metal concentration can also occur at WWTWs. For example, Chipasa (2003), who investigated the occurrence of metals in a WWTWs located in Gdansk (Poland) over a two-year period, observed a wide variation in influent metal concentrations between months, which was particularly pronounced for Cu and Zn.

The variability in inputs means it is difficult to quantify trace metal fluxes to WWTWs and, in many instances, there is insufficient evidence to identify metal sources. Moreover, WWTWs operators have limited ability to directly control the concentration

of contaminants reaching works and, as such, an understanding of metal sources is often insufficient to be used to reduce metal inputs (Ziolko et al. 2011). Therefore, it is of greater importance to understand the behaviour of metals in wastewater. Most of the studies currently available report total metal concentrations, with limited details about their speciation and phase distribution, two important parameters which influence metal fate in wastewater treatment.

Table 2.2 Metal concentrations ($\mu\text{g/L}$) in influent [Mean (SD)].

Location	Cu	Pb	Ni	Zn	Reference
Thessaloniki, Greece (n = 9)	79 (35)	39 (9)	77*	470 (140)	[1]
Ribeirao Preto, Brazil (n = 29)	17 (5)	37 (60)	-	79 (41)	[2]
5 WWTWs, Italy**					[3]
WWTW A (70% Ind)	32 (19)	7 (29)	17 (75)	254 (42)	
WWTW B	10 (56)	8	4 (31)	348 (31)	
WWTW C	10 (44)	9	17 (23)	1233 (20)	
WWTW D (37% Ind)	38 (61)	2 (60)	62 (4)	2411 (29)	
WWTW E (6% Ind)	61 (39)	11 (27)	22 (60)	227 (37)	
Nancy, France (n = 15)	59 (36)	6 (4)	7 (3)	140 (65)	[4]
3 WWTWs, Wisconsin, US					[5]
Jackson	71	7	7	89	
Madison	70	7	12	115	
Medford	107	8	6	111	
Milwaukee, US (n \geq 234)	73 (2)	11 (1)	11 (0.4)	164 (3)	[6]
30 WWTWs, UK	78	25	14	155	[7]
16 WWTWs, UK (n = ~150)	76 (48)	17 (16)	14 (10)	180 (72)	[8]
Melbourne, Australia	62 (15)	13 (7)	4 (2)	169 (76)	[9]

* personal communication with C. Samara reported by Ziolko et al. (2011). ** Mean (variation coefficient %). [1] Karvelas et al. (2003), [2] da Silva Oliveira et al. (2007), [3] Carletti et al. (2008), [4] Houhou et al. (2009), [5] Shafer et al. (1998), [6] Soonthornnonda and Christensen (2008), [7] Rule et al. (2006), [8] Gardner et al. (2013), [9] Wilkie et al. (1996).

2.5. Fate of metals in municipal wastewater treatment

Municipal WWTWs are designed to control a wide range of determinands, such as solids, nutrients, biological oxygen demand (BOD) and pathogens. While these constituents can be efficiently and consistently eliminated, the removal of metals is often insufficient. Hence, the evaluation of the fate and removal of trace metals during wastewater treatment is important for the optimisation of treatment processes, and to

inform the selection of alternate treatment techniques to enhance trace metal removal where this is required.

2.5.1 Primary treatment

Primary sedimentation tanks contribute toward the overall rate of removal of metals in municipal WWTWs. The metal removal process in the primary treatment stage is physical and the rate of removal depends upon whether the metal is present in insoluble form (i.e. associated with particulate materials). Metal size distribution is therefore a key factor influencing metal removal at this treatment stage.

2.5.1.1 Metal size distribution in primary treatment

Metals are traditionally considered to exist in two size fractions: a soluble fraction that passes through a 0.45 μm filter and the corresponding particulate fraction retained on the filter (i.e. $> 0.45 \mu\text{m}$). Each metal behaves differently in wastewater and studies reporting the distribution of metals between these fractions in influent have revealed that Cu and Pb are predominantly found in particulate form (see Table 2.3). Such behaviour indicates their presence as insoluble species, an observation supported by removal correlations with TSS (Inna et al. 2014). For Ni, $> 50\%$ distribution in the soluble fraction of influent at municipal WWTWs was reported (see Table 2.3). In addition, low stability constants for Ni complexes mean that this metal is the most mobile in wastewater (Ščančar et al. 2000; Sörme and Lanqvist, 2002). Thus, Ni is not readily removed in conjunction with suspended particles (Karvelas et al. 2003). Zn is also mobile in wastewater, however higher stability constants for Zn complexes and affinity for TSS in wastewater means a substantial proportion of Zn is typically found in the particulate fraction (Table 2.3).

The size distribution of metals may be affected by many parameters, including influent metal and TSS concentrations as well as pH and redox potential. All these parameters are interrelated and are highly site specific and may ultimately impact upon the rates of removal for metals (Lester, 1983; Lawson et al. 1984a; Lester, 1987). As shown in Table 2.3, distribution of metals between particulate and soluble fractions can vary between sites. Ziolkó et al. (2009) who investigated the partitioning of Cu at eight

WWTWs in North West England reported that the soluble fraction accounted for between 7% and 30% of total Cu in influent. Studies elsewhere (Goldstone et al. 1990a,b) have also shown temporal variation at WWTWs. Nevertheless, most studies agree that Cu, Pb and Zn are predominantly found in the particulate fraction of influent and that Ni is primarily distributed in the soluble fraction (Table 2.3).

Table 2.3 Distribution (%) of metals in the soluble fraction of influent.

Location	Cu	Pb	Ni	Zn	Reference
9 WWTWs, France	24	18	57	25	Choubert et al. 2011
Paris, France	<27	<27	78	<27	Buzier et al. 2006
Nancy, France	34	27	94	41	Houhou et al. 2009
16 WWTWs, UK	30	12	65	23	Gardner et al. 2013
8 WWTWs, UK	7-30	-	-	-	Ziolko et al. 2009
Norwich, UK	9	~15	71	35	Goldstone et al. 1990a,b

The soluble fraction of wastewater contains DOC with functional groups (ligands) that may complex metal ions. Binding of metals to dissolved ligands reduces their affinity for settleable particles and thus enhances their mobility (Ziolko et al. 2011). DOC is known to pass through primary treatment stage unaltered, for example Katsoyiannis and Samara (2007) observed a mean removal rate of 0.8% at Thessaloniki WWTWs. It is therefore acknowledged that metal complexed with dissolved organic constituents are unaffected by the primary sedimentation process. Synthetic ligands including nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA) are also distributed in the soluble fraction of wastewater and can influence metal removal (Shon et al. 2006; Almutairi and Lovitt, 2012).

2.5.1.2 Metal removal in primary treatment

Primary treatment processes aim to remove suspended solids from influent wastewater, therefore removal of metals in the soluble fraction is scarce within primary treatment, as indicated by increases in the ratio of soluble to particulate metal observed in primary effluent (Karvelas et al. 2003). Settling of particulates is, thus, the predominant removal mechanism within primary treatment. In primary settlement tanks, settlement generally takes place near the surface and the process is strongly influenced by the size of

particulates, such that, the rate of settling positively correlates with particle size. The rate of settlement can be enhanced by flocculation, a mechanism which involves the agglomeration of particles into larger aggregates which settle at a faster rate (Tchobanoglous et al. 2014). The flocculation process occurs spontaneously in the lower section of primary settlement tanks and can be improved through the application of chemical reagents that can enhance TSS as well as metals removal (Johnson et al. 2008).

Metals which are predominantly insoluble in influent, such as Cu and Pb (Table 2.3), are typically well removed in conjunction with suspended particles during primary treatment (Buzier et al. 2006; Ziolkowski et al. 2009; Inna et al. 2014) with rates of removal > 70% observed (see Table 2.4). Primary treatment can also remove Zn moderately, with removals up to 73% recorded (Table 2.4). For Ni, removals in primary treatment are typically below 25% and are lower than those observed for other metals (Table 2.4). Nevertheless, in some instances, comparable removal rates for Cu, Pb, Ni and Zn were found in primary settling tanks (Goldstone et al. 1990a,b; Karvelas et al. 2003). This indicates that when present in particulate form, Ni can readily settle. Thus highlighting that for metals to be removed in primary treatment they must be insoluble and bound to readily settleable particulates.

Table 2.4 Rates of removal (%) reported in primary treatment at different WWTWs worldwide (Mean).

Location	Cu	Pb	Ni	Zn	Reference
Thessaloniki, Greece	27	21	22	19	Karvelas et al. 2003
Jackson, US	84	31	12	-4	Shafer et al. 1998
Paris, France	40	73	22	-	Buzier et al. 2006
Canada	70	59	-	68	Oliver and Cosgrove, 1974
Norwich, UK	59	71	71	73	Goldstone et al. 1990a,b

2.5.1.3 Operating parameters influencing metal removal in primary treatment

2.5.1.3.1 Hydraulic retention time

During primary treatment, improvements in metal removal can be achieved by optimising operating conditions. Hydraulic retention time (HRT) is the amount of time

that allows for flocculation and settling in primary treatment to occur. Metals that are strongly associated with particulate matter will consequently experience increased rates of removal with increasing HRT. In most cases, however, extending HRT at WWTWs would require costly infrastructure developments (Petrie et al. 2014) and consequently other solutions may be preferred.

2.5.1.3.2 Sludge returns

Sludge returns are complex organic mixtures containing additional colloids that drive the flocculation process within settling tanks (Buzier et al. 2006). Returns at WWTWs typically contain high particulate concentrations of Cu, Pb, Ni and Zn (Inna et al. 2014), and can exert a large degree of impact upon primary treatment loading. Ziolkowski et al. (2009) reported that Cu concentrations in returned liquors were up to two orders of magnitude greater than those observed in the influent and contributed between 27 and 66% to the total load of this metal in primary sedimentation. Returns are also known to carry high concentrations of TSS, which can initiate the partitioning of soluble metals onto the surface of solid particles (Buzier et al. 2006), thus increasing the rate of metals removal. Variability within rates of removal in primary treatment (Table 2.4) demonstrates that site specific parameters including nature and type of returned liquors influence the rates of metal removal. For example, Ziolkowski et al. (2009) observed that in different return streams and at different sites for the same return, the concentrations of Cu were highly variable.

2.5.2 Biological treatment

Biological treatments can be separated into two distinct processes: a biological reactor and a phase separator (Lester, 1987). Two conventional processes can be employed in biological reactors: suspended growth (activated sludge [AS]) or attached growth (trickling filter [TF]) (Tchobanoglous et al. 2014). In these processes, micro-organisms (primarily bacteria) oxidise biodegradable particulate and soluble organic matter in wastewater into carbon dioxide, water and additional biomass, which is later consolidated in secondary sedimentation tanks (Tchobanoglous et al. 2014). Although biological treatment is designed to eliminate organic matter, it also has the capacity to remove suspended particles and soluble metal from wastewater.

2.5.2.1 Mechanisms of metal removal in biological treatment

In AS and TF treatment processes, biomass traps fine particulates which then settle with sludge flocs facilitating the removal of insoluble metal in conjunction with suspended particles (Liu et al. 2001). Biomass also produces and secretes extracellular polymeric substances (EPS) that are mainly composed of polysaccharides and proteins, containing functional groups such as hydroxyl, carboxyl and amine groups (Liu and Fang, 2002). These groups serve as potential binding sites for the sequestration of metal ions (Brown and Lester, 1982a,b; Liu and Fang, 2002). The mechanism of metal biosorption involves a physico-chemical interaction between the functional groups on the cell surface and the metal, based on ion exchange, complexation, coordination, chelation, physical adsorption, and microprecipitation (Ledin, 2000; Volesky, 2001). These mechanisms act simultaneously to varying extents depending on the solution environment, biomass composition, surface properties and functional chemical groups (Volesky, 2001; Mudhoo et al. 2012). The distribution of metals within the soluble fraction of wastewater is also an important factor influencing metal removal in biological treatment.

2.5.2.2 Metal size distribution in biological treatment

Advances in particle size fractionation has allowed the soluble fraction to be separated into two further phases: a colloidal fraction, which encompasses material found in the size range 1 kDa to 0.45 μm , and a truly dissolved fraction, which is composed of constituents with a molecular weight < 1 kDa (Worms et al. 2010a; Gagnon et al. 2014). It has been reported that the distribution of metals between colloidal and truly dissolved fractions is strongly influenced by the distribution of DOC between such fractions (Worms et al. 2010a). In effluent, the colloidal fraction is mainly composed of macromolecules including polysaccharides and proteins, which readily complex metals owing to their large binding site density and polyfunctional character (Jarusutthirak et al. 2002; Worms et al. 2010a). The truly dissolved fraction is composed of hydrated metal ions as well as low molecular weight organic constituents (such as amino acids and carbohydrates) and synthetic ligands (such as NTA and EDTA) to which metals can complex with (Imai et al. 2002; Shon et al. 2006). Removal of macromolecular (colloidal) constituents from wastewater is favoured, as their large number and diversity

of functional groups enhances attachment to precipitates (Haberkamp et al. 2007). In addition, materials with higher molecular weight can more readily overcome electrostatic repulsion to become adsorbed (Wang et al. 2015). Conversely, synthetic ligands are not typically degraded by biological processes (Kari and Giger, 1996; Nirel et al. 1998), thus metals complexed to them may not be adsorbed and may subsequently be released in effluent discharges.

Metals such as Cu and Pb can adsorb onto the surface of colloidal materials (Martin et al. 1995). For example, Shafer et al. (1998) observed that 30% of total Cu was distributed in the colloidal fraction (10 kDa – 0.22 μ m) in effluent from Madison WWTWs (US). Conversely, since Ni and Zn are highly soluble in wastewater and, given what is understood of their thermodynamic properties (i.e. slow rate of reaction, low stability constants), a large proportion of soluble Ni and Zn would be expected to remain unbound in the free ionic form and therefore found in the truly dissolved size fraction. This assumption has, however, been challenged by others (Worms et al. 2010a,b) who have reported that Ni and Zn can interact with organic materials in the colloidal fraction. However, DOC is seldom measured in WWTWs (Katsoyiannis and Samara, 2007) and the influence DOC has on the behaviour of metals in wastewater is not well understood (Worms et al. 2010a). In addition, inorganic metal complexes may also be present in wastewater. Nevertheless, studies investigating the size distribution of metals in wastewater treatment are limited to conventional classification (i.e. soluble and particulate). This simplistic approach restricts our understanding of the mechanisms influencing metal fractionation, limiting the design and performance of wastewater treatment processes.

2.5.2.3 Metal removal in biological treatment

Rates of removal recorded at WWTWs worldwide are presented in Table 2.5, which shows wide variation between sites operating both AS and TF treatment types. In fact, overlapping variation indicates that these biological processes achieve similar removal performance. As in primary treatment, characteristics of the metals play a significant role in their removal. Cu yielded the highest removal rate followed by Pb, Zn and Ni (Table 2.5). In biological treatment large amounts of TSS are typically removed from

wastewater (Table 2.5); hence, settlement of insoluble metal with the sludge in the secondary sedimentation tank is an important removal pathway (Sterritt et al. 1981).

Table 2.5 Removal rates (%) reported in biological treatment at WWTWs worldwide [Total (Soluble)].

Location	Cu	Pb	Ni	Zn	TSS	Ref.
TF Treatment Works						
North West England						[1]
WWTW 1	22 (-76)	-	-	-	-	
WWTW 2	52 (17)	-	-	-	-	
WWTW 3	71 (16)	-	-	-	-	
WWTW 4	50 (-5)	-	-	-	-	
WWTW 5	55 (-94)	-	-	-	-	
WWTW 6	52 (-7)	-	-	-	-	
WWTW 7	44 (-17)	-	-	-	-	
UK						[2]
WWTW 1	-3 (1)	-22	-29 (-7)	-10 (-5)	34	
WWTW 2	59 (-176)	41	27 (18)	45 (14)	86	
WWTW 3	8 (-67)	-10	29 (31)	34 (-14)	64	
WWTW 4	25 (-23)	24	2 (3)	27 (-9)	76	
WWTW 5	-20 (-17)	33	-18 (25)	-7 (-7)	33	
WWTW 6	49 (47)	28	25 (21)	26 (-11)	77	
WWTW 7	49 (3)	69	6 (7)	52 (18)	46	
Mean	37 (-28)	24	6 (14)	24 (14)	59	
Standard Deviation	26 (57)	31	23 (13)	24 (22)	22	
AS Treatment Works						
UK						[2]
WWTW 8	88 (76)	83	38 (-1)	47 (-58)	91	
WWTW 9	82 (83)	95	25 (-10)	86 (16)	97	
WWTW 10	91 (85)	79	31 (20)	44 (-37)	96	
WWTW 11	89 (81)	74	25 (13)	49 (-28)	95	
WWTW 12	86 (81)	82	24 (5)	64 (14)	93	
WWTW 13	80 (70)	95	35 (13)	61 (18)	94	
WWTW 14	79 (40)	85	48 (11)	82 (3)	87	
Norwich, UK	61 (-97)	31	15	15	-	[3,4]
North West England	94 (50)	-	-	-	-	[1]
Canada	60 (56)	79 (50)	1 (<1)	50 (30)	-	[5]
Los Angeles, US*	77 (12)	53 (44)	41 (32)	59 (-97)	-	[6]
Thessaloniki, Greece	43	13	44	29	96	[7]
Mean	78 (49)	70	30 (9)	53 (-15)	94	
Standard Deviation	15 (53)	27	14 (12)	21 (43)	3	

*Soluble fractions are those remaining in filtrate after filtration through 0.2 µm membrane filters. [1] Ziolkowski et al. (2009), [2] Gardner et al. (2013), [3] Goldstone et al. (1990a), [4] Goldstone et al. 1990b, [5] Oliver and Cosgrove (1974), [6] Chen et al. (1974), [7] Karvelas et al. (2003).

Adsorption of soluble metal species onto the surface of biomass is also an important metal removal mechanism, with removal of soluble metals observed at many of the sites

that have been investigated (see Table 2.5). The data from the table illustrates that removal of soluble metals does not follow a typical trend, with extremely high variability in removals between sites. In fact, at several works negative removal rates have been recorded for Cu, Pb, Ni and Zn, indicating that solubilisation can occur in biological treatment (Table 2.5). Solubilisation of Cu and Pb has also been observed by other researchers (Lawson et al. 1984a,b; Rudd et al. 1984) when simulating the AS process at laboratory scale, and it has been suggested that the cause of such occurrence may be the oxidation of extracellular polymers which can initiate the release of metal ions into effluent.

Overall, data presented in Table 2.5 indicate that metal removal by conventional biological treatments is vagarious, and removal of metals from the soluble fraction of wastewater is a major challenge at WWTWs (Santos and Judd, 2010; Gardner et al. 2013). Variation in metals removal may result from several factors, namely physicochemical characteristics such as pH, temperature, particle size and metal concentration, and the concentration of extracellular materials (Ziolko et al. 2011). Similarly to primary treatment operational conditions, in particular retention times, are also influential and may be controlled to optimise metal removal.

2.5.2.3.1 Influence of retention time

Increasing HRT in TFs is known to increase the removal of TSS and organic materials from wastewater (Almeida et al. 2013). Given that metals can be associated with these constituents, longer HRTs may increase the removal of metals in TF treatment. There is however a paucity of published work reporting data on the performance of TFs at varying HRTs.

Residence times in TFs typically vary from 3 to 60 min, whereas in the AS process retention times between 120 and 480 min or longer are required (Scholze, 1988). In the AS process, sludge retention time (SRT) controls the size and diversity of a microbial community. Longer SRTs enhance bacterial species quantity and diversity as well as favour the survival rate of autotrophic nitrifying bacteria. These conditions stabilise microbial communities within sludge enabling the formation of small, spherical and compact flocs. Such characteristics increase floc surface area and the subsequent

availability of binding sites for metal sorption (Laurent et al. 2009). Enhanced removal of Cu, Pb, Ni and Zn can therefore be achieved by extending SRTs. For example, on increasing SRT from 3 to 27 days Petrie et al. (2014) recorded an increase in the removal rate for Cu from 38 to 82%. Following an increase in SRT from 11 to > 1000 days, the removal rates of Pb and Ni increased from 89 and 40% to > 98 and 50% respectively (Cecchi et al. 2003; Fatone et al. 2005; Fatone et al. 2008). Whereas, for Zn, removal rates have been reported to increase from 51 to 94% when enhancing SRT from 10 to > 300 days (Innocenti et al. 2002; Cecchi et al. 2003; Conklin et al. 2007). Nevertheless, conflicting studies have shown the removal of Cu and Pb to decrease upon increasing SRT (Innocenti et al. 2002; Cecchi et al. 2003; Fatone et al. 2008). Explanations for such occurrences include the concomitant increase in organic matter (Innocenti et al. 2002; Cecchi et al. 2003) or the solubilisation of metals, as has been observed in the AS process (Lawson et al. 1984a,b; Rudd et al. 1984).

The uncertainty in the literature of the performance of biological treatments at increasing retention time means it is debatable whether this operational solution is suitable to enhance metal removal at WWTWs. Especially given that longer retention times are correlated with increasing costs (Amanatidou et al. 2015) and spatial requirements. There is, therefore, a strong likelihood that to achieve increasingly stringent discharge requirements, the application of advanced treatment technologies will be required at municipal WWTWs.

2.6. Advanced treatment technologies to enhance trace metal removal in municipal wastewater treatment

The following section presents an overview of the current treatment options that have demonstrated the capability to remove metals from wastewater with initial concentrations ≤ 1 mg/L.

2.6.1 Coagulation-flocculation

Coagulation-flocculation (CF) is used for the removal of particulate, colloidal and in some instances dissolved substances (Luo et al. 2014). Coagulation involves the addition of chemical reagents which combine insoluble particles and dissolved organic

matter into larger aggregates (Renault et al. 2009). Flocculation consists of a stirring or agitation procedure that encourages particles to agglomerate, which allows their removal in subsequent filtration or sedimentation phases (Renault et al. 2009). Mechanisms through which particulate and colloidal materials aggregate depend on the type of reagent used. Chemical reagents frequently applied in the CF process include metal salts, such as ferric chloride (FeCl_3) and polyaluminium chloride (PAC), and synthetic polymers such as polyacrylamide. Metal salts remove particles by charge neutralisation and by enmeshment of particles in a growing hydroxide precipitate (Duan and Gregory, 2003). El Samrani et al. (2008) employed either FeCl_3 or PAC for the removal of metals from combined sewer overflow (with initial concentrations between 25 and 160 $\mu\text{g/L}$); this resulted in excellent elimination of Cu, Pb and Zn around optimum coagulant concentrations. Conversely, at Seine-Aval WWTWs (France), Buzier et al. (2006) revealed that FeCl_3 was responsible for increasing the Ni concentration in effluent due to impurities; similar findings have been reported in studies elsewhere (Chys et al. 2013). Synthetic polymers aggregate particles by inter-particle bridging. This mechanism involves the sorption of particles onto polymeric chains. The loops and tails of adsorbed polymeric chains extend and attach onto the surface of other particles, enabling bridging of particles to occur (Shak and Wu, 2014).

Studies reporting the application of synthetic polymers and metal salts for metal removal in municipal wastewater treatment are limited. This could be in part due to their environmental consequences, which include significant alteration to the pH of treated wastewater and the production of voluminous toxic sludge (Renault et al. 2009; Vijayaraghavan et al. 2011). For example, Sotero-Santos et al. (2005) found that FeCl_3 sludge caused chronic toxicity, demonstrated by low fecundity and mortality of *Daphnia similis*, whilst consumption of Al species may lead to Alzheimer's disease (Dassanayake et al. 2015). For these reasons, alternative reagents have been considered for coagulation-flocculation. Biopolymers are of significant interest since they are natural low-cost products with environmentally friendly characteristics including no toxicity, biodegradability and produced from a renewable resource (Renault et al. 2009). A large body of literature has investigated the application of biopolymers for metals removal. Agents such as chitosan, Tanfloc and *Moringa oleifera* have been found to remove effectively at least two of the following metals; Cu, Pb, Ni and Zn from

synthetic solutions (Beltrán Heredia and Sánchez Martín, 2009; Kalavthy and Miranda, 2010; Shaheen et al. 2013). Despite such findings and the fact that coagulation-flocculation is a simple low-cost technology, the ability of biopolymers to remove metals at concentrations present in municipal wastewater remains unexplored.

2.6.2 Adsorption

Adsorption is a mass transfer process involving the transfer from the liquid phase onto the surface of a solid (adsorbent) of a desired substance (adsorbate) which can be bound by a chemical or physical interaction (Kurniawan et al. 2006). Offering flexibility in design and operation and is capable of producing high-quality effluent, adsorption is widely recognised to be effective and economic for the removal of metals from wastewater (Fu and Wang, 2011).

2.6.2.1 Activated carbon adsorbents

Activated carbon (AC) adsorbents are commonly used to enhance the removal of metals. Its use derives from large density of meso and micropores and the subsequent large surface area (Fu and Wang, 2011). In spite of its prolific use, AC is an expensive material and requires complexing agents to improve performance for the removal of inorganic materials (Babel and Kurniawan, 2003). Such costs mean AC is no longer attractive for use in wastewater treatment. In fact, the search for low-cost and easily available adsorbents to remove metals has become a focus of many research studies (Fu and Wang, 2011). Despite the hundreds of published studies which have investigated the use of low-cost industrial by-product, household, agricultural and biological sorbents, few have investigated the ability to remove metals from municipal wastewater at real world conditions. Those available have revealed biosorbents including microorganisms and aquatic plants as promising agents to enhance metal removal.

2.6.2.2 Adsorption by microorganisms

Microorganisms studied for metals removal include, fungi, bacteria and algae. Algae are considered the most desirable microorganisms for use as biosorbents as they possess several advantages. Since they are autotrophs, algae require minimal nutrients to produce large biomass and are less likely to produce toxins when compared with fungi

and bacteria (Wang et al. 2010). Furthermore, owing to their large surface area and high binding affinity, algae have been reported to be more effective at sequestering metal species compared with bacterial and fungal biomass (Roy et al. 1993; Khoshmanesh et al. 1996). Algal surfaces (mucilage/cell wall) contain different functional groups such as hydroxyl, carboxyl and sulphate groups found in their carbohydrate, lipid and protein components (Crist et al. 1992). Different algal species have different shapes, sizes and compositions, all of which influence their metal binding rate (Tam et al. 1997). In a recent study, Zhou et al. (2014) studied the removal of various metals from wastewater (initial concentrations – Pb: 1.03 µg/L, Ni: 6.21 µg/L, Zn: 149.66 µg/L) by four species of freshwater green algae: *Chlamydomonas reinhardtii*, *Scenedesmus obliquus*, *Chlorella pyrenoidosa* and *Chlorella vulgaris*. For Zn, removals were substantially different between algae species, ranging from 39% for *Chlamydomonas reinhardtii* to 93% for *Scenedesmus obliquus*. Nevertheless, low removal rates (11-39%) were calculated for Pb and Ni among the four algae species. In fact, in most instances the following removal trend was identified Zn > Ni > Pb. These findings indicate that the removal of metals was determined by metal species, with surface complexation and ion exchange identified as the major removal pathways.

The main challenge for the application of algae in wastewater treatment is harvesting, which ensures good effluent quality (i.e. low TSS concentrations) and prevents cell washout during operation (Evans and Furlong, 2003). Although harvesting can be effectively accomplished by techniques such as centrifugation or filtration, these processes can be expensive and difficult to implement. Hence, despite their efficiency for the removal of metals, the use of algae remains limited by such difficulty (Muñoz and Guieysse, 2006).

2.6.2.3 Adsorption by aquatic plants

Phytoremediation is the removal of pollutants by the use of plants, which offers promise for the removal of metals from wastewater (Mishra and Tripathi, 2008). Of particular interest in this regard are macrophytes that have accumulator phenotypes for one or several metals and can accumulate them in concentrations 100,000 times greater than those in associated waters (Kamal et al. 2004; Mishra and Tripathi, 2008). These plants are thought to accumulate and subsequently remove metals in several ways including

(1) attachment to the cell wall, (2) accumulation in the roots and (3) hyperaccumulation. The ability of macrophytes to accumulate metals makes them an essential component in CWs, treatment technologies which are considered cost-efficient, effective and environmentally friendly (Brix, 1997; Stottmeister et al. 2003).

2.6.3 Horizontal subsurface flow constructed wetlands

Horizontal subsurface flow (HF) CWs are large gravel or sand filled basins planted with wetland vegetation. In this process, wastewater flows horizontally through the basin until reaching the outlet. HFCWs can effectively remove suspended solids and organic matter (Pedescoll et al. 2015) and have the capacity to enhance metal removal. As well as uptake by plants, processes responsible for metal removal also include precipitation as insoluble salts (mainly oxyhydroxides and sulphides) and binding to sediments and soils. A number of studies have revealed HFCWs to be effective for the removal of metals from municipal wastewater (see Table 2.6). The results indicate that metals are removed at various rates, with Cu, Pb and Zn typically removed to a greater extent compared with Ni.

Table 2.6 Total metal removal from municipal wastewater by HFCWs (Mean).

Location	Plant species	Metal	Initial conc. (µg/L)	Removal (%)	Reference
Břehov, Slovakia	<i>Phragmites phalaris</i>	Cu	40	84	Kröpfelová et al. 2009
		Pb	13	78	
		Ni	22	46	
		Zn	186	86	
Mořina, Czech Republic	<i>Phragmites phalaris</i>	Cu	25	74	
		Pb	16	84	
		Ni	18	49	
		Zn	232	91	
Slavošovice, Czech Republic	<i>Phragmites</i>	Cu	25	42	
		Pb	4	26	
		Ni	6	-12	
		Zn	72	58	
Zemst, Belgium	<i>Phragmites australis</i>	Cu	21	88	Lesage et al. 2007
		Pb	11	67	
		Ni	7	36	
		Zn	122	86	
León, Spain	<i>Phragmites australis</i>	Cu	21	84	Pedescoll et al. 2015
		Pb	5	88	
		Ni	5	12	
		Zn	59	87	

The characteristics of metal types significantly influence their removal by CWs. Cu readily forms very insoluble compounds with sulphur (Sobolewski, 1999), as Pb and Zn do with sulphide and carbonate (Lin, 1995; Stumm and Morgan, 2012). Cu and Zn are also co-precipitated with Fe and Mn oxides (Stumm and Morgan, 2012). Although Ni can form sulfide and carbonate precipitates and can co-precipitate with Fe and Mn oxides (Vymazal and Kröpfelová, 2008), rates of removal for this metal in HFCWs can vary widely (Kröpfelová et al. 2009) as shown in Table 2.6. Cu and Zn are also accumulated in plants to a much greater degree than other metal types. Cu is important for cell function and is essential in the structural stability of energy transfer processes and chromosomes (Pahlsson, 1989). Whereas, Zn is an essential element affecting enzyme activity and fundamental metabolic processes (MacFarlane and Burchett, 2002). On the other hand, Ni is required least for plant metabolism and as such has been revealed to accumulate to a lesser degree in plant tissues relative to other metal types (Upadhyay et al. 2007).

Rates of removal at CWs are strongly dependant on influent metal concentrations. For example, in the study by Kröpfelová et al. (2009) rates of removal were similar at Břehov and Mořina HFCWs, whilst at Slavošovice values were substantially lower, as were the initial metal concentrations in most cases (Table 2.6). Furthermore, low inflow concentrations of suspended solids and organics (COD, BOD₅), and lower sediment build up in the filtration bed at the Slavošovice site could have influenced metal removal. Lower sediment levels (~50%) compared with CWs at Břehov and Mořina could reduce retention via metal complexation with organic compounds. In addition, the variety of processes responsible for metal removal in CWs (i.e. precipitation, plant uptake, sedimentation) are directly or indirectly influenced by different internal and external environmental conditions, including, temperature, redox conditions, availability of dissolved oxygen and operation strategies.

CWs are land intensive and this remains a substantial barrier to their widespread application, especially in densely populated areas where land prices are often too high (Zhang et al. 2014) and the required space is not available.

2.6.4 Membrane bioreactor

Developments in membrane technology and understanding of the filtration mechanism, has led to MBR technology becoming a feasible treatment for the removal of metals from municipal wastewater. MBR systems involve a combination of AS (biological) treatment and membrane filtration (microfiltration, MF or ultrafiltration, UF). MBRs possess many advantages over conventional biological treatments including high effluent quality, high biomass content and small footprint (Luo et al. 2014). SRT is an important parameter influencing metal removal in biological treatment (see section 2.5.2.3.1) and enhanced removal rates for metals can be achieved with extended SRTs (Santos and Judd, 2010). Since a higher SRT is typically found in a MBR compared with AS treatment, rates of removal can be higher in the former. In a study by Santos and Judd (2010), MBRs were found to deliver a slightly greater removal rate (up to an 18% increase for target metals in this study) compared with conventional AS systems, whilst increases between 10 and 15% were recorded elsewhere by Bolzonella et al. (2010). Nonetheless, it has been suggested that increased concentrations of dissolved organics at higher SRTs within MBRs may promote dissolution of metals (Malamis et al. 2009). For example, Crane et al. (2010) found that MBRs achieved inferior removals of Cu and Zn when compared with AS and TF treatments, owing to the production of organic molecules able to chelate and subsequently retain Cu and Zn. Other studies have also shown Cu and Pb removal rates to decrease at increasing SRT (Innocenti et al. 2002; Cecchi et al. 2003; Fatone et al. 2008), whilst Ni removal is known to be unaffected by this operating parameter (Fatone et al. 2008). Given these findings and the high energy and voluminous waste MBRs generate, it is debatable whether the selection of this technology is justifiable to enhance metal removal (Santos and Judd, 2010).

2.6.5 Microfiltration and ultrafiltration

MF and UF can be used as a tertiary filtration, rather than in an MBR configuration where the filter is submerged in the AS. The process configuration should be considered as tertiary filtration and MBRs have different capital and operational costs (Cotè et al. 2004; Judd, 2006). In a comparative study, Battistoni et al. (2007) investigated the effectiveness of an UF membrane in both configurations for the removal of Cu, Pb and Ni from wastewater (with initial concentrations between 18 and 265 µg/L). Although

findings revealed satisfactory metals removal (17–70%) for the tertiary filtration configuration, the MBR technique achieved higher removals (with increases in the range 8 to 47%). This suggests that the fouling or cake layer on the membrane may contribute toward the removal of metals in the liquid phase (Battistoni et al. 2007). The fact remains, however, that MF and UF technologies in MBRs and in effluent filtration are unlikely to achieve desired metal concentrations to comply with increasingly stringent discharge quality requirements. They are, nonetheless, a suitable pre-treatment to nanofiltration (NF) or reverse osmosis (RO) technologies.

2.6.6 Nanofiltration

The separation mechanism in NF involves steric (sieving) and electrical (Donnan) effects (Kurniawan et al. 2006). A Donnan potential is created between charged ions in the NF membrane and co-ions in the effluent, with the latter rejected (Van der Bruggen and Vandecasteele, 2003). A number of factors are known to influence removal rates for NF membrane processes. These include (1) wastewater characteristics such as pH, ionic strength and organic matter concentrations, (2) physio-chemical characteristics of metals including metal size distribution, and (3) membrane characteristics, such as zeta potential, contact angle, roughness and molecular weight cut off (MWCO) (Bellona and Drewes, 2005).

It is, however, recognised that the prominent factor influencing removal is the MWCO of the membrane. In a study by Chon et al. (2012), Ni and Pb were not effectively removed by 1000 Da or 350 Da membranes, whereas good rates of removal were recorded for Pb, Ni and Cu when municipal wastewater was treated with a 210 Da membrane (see Table 2.7). In fact, commensurate findings for 210 Da membranes were also reported in an earlier study by Chon et al. (2011), the findings of which are shown in Table 2.7.

A comparative study of the removal of Cu, Zn and Ni from municipal wastewater by NF or RO was undertaken by Garcia et al. (2013). At similar initial metal concentrations (see Table 2.7), removal rates of approximately 98% were reported for Cu, Zn and Ni, whilst, as shown in Table 2.7, similar removal rates were attained for these metals with RO. These results show that RO and NF can effectively remove metals from municipal

wastewater. However, NF requires a lower operating pressure compared with RO, therefore is preferred due to its lower treatment costs (Mohammad et al. 2004).

Table 2.7 Metal removal from municipal wastewater by NF or RO (Mean).

Membrane Process	Metal	Initial conc. (µg/L)	Mean Removal (%)	Conditions	Reference
NF	Cu	79.58	66	MWCO = 1000 Da	Chon et al. 2012
	Pb	2.05	14		
	Ni	16.45	-2		
NF	Cu	79.58	79	MWCO = 350 Da	
	Pb	2.05	-169		
	Ni	16.45	28		
NF	Cu	79.58	87	MWCO = 210 Da	
	Pb	2.05	69		
	Ni	16.45	82		
NF	Cu	245.5	93	TMP* = 413.7 kPa MWCO = 210 Da	Chon et al. 2011
	Pb	2.7	96		
	Ni	16.5	96		
	Zn	992.6	91		
NF	Cu	14.6 – 65.6	~ 98	TMP = 400 kPa	Garcia et al. 2013
	Zn	43.3 – 194.7	~ 97		
	Ni	7.6 – 34.1	~ 98		
RO	Cu	19.9 – 89.7	~ 99	TMP = 900 kPa Low energy	
	Zn	22.1 – 99.5	~ 95		
	Ni	4.3 – 19.3	~ 99		
RO	Cu	8 – 35.9	~ 99	TMP = 900 kPa High rejection	
	Zn	27.2 - 122.5	~ 97		
	Ni	3.7 – 16.5	~ 98		
RO	Cu	2.8	-	TMP = 1400 – 1600 kPa	Malamis et al. 2012
	Pb	24.9	-		
	Ni	3.7	-		
	Zn	117.8	> 99		
RO	Cu	BDL** – 38.7	99.99	TMP = 1520 kPa	Dialynas and Diamadopoulos, 2009

*Transmembrane pressure. **Below detection limit.

2.6.7 Reverse osmosis

The RO process utilises a semi-permeable membrane which allows the fluid that is being purified to pass through, while rejecting pollutants (Fu and Wang, 2011). RO is capable of removing a wide range of dissolved species from water, and is an increasingly popular technology for the treatment of wastewater. The use of RO systems to remove metals from municipal wastewater has been investigated by a number of researchers (see Table 2.7). Malamis et al. (2012) revealed that the RO system achieved

complete removal (below the limit of detection, $< 0.9 \mu\text{g/L}$) of Cu, Pb and Ni from municipal wastewater, whilst the mean removal rate for Zn was $> 99\%$. Garcia et al. (2013) applied a pilot-scale RO system and observed mean removal rates between 94.5 and 99% for Cu, Ni and Zn. This study also investigated the fate of metals at a full-scale MF-RO works operating in the UK. Results indicated slightly lower removal rates for the RO process (91-97%) owing to the adverse effects of membrane ageing. Restoration of the membranes and pumping pressures mean high energy consumption requirements, and this is the main drawback for RO application (Fu and Wang, 2011). Additionally, management of the retentate stream would incur further management costs.

Even though NF requires a much lower operating pressure compared with RO (see Table 2.7), the high costs of membrane replacement still remain when operating this technique. Furthermore, it is also important to remember that NF and indeed RO require wastewater to be pre-treated (by for example MF or UF) to remove suspended materials.

2.7 Concluding remarks

Requiring an improved quality of treated effluent, environmental regulations are becoming increasingly stringent. Bioavailability-based standards are expected to significantly reduce acceptable metal concentrations. In general source control is no longer a feasible option, owing to the increasing relevance of diffuse metal sources. As such, WWTWs may require the optimisation of conventional treatment processes or the implementation of advanced treatment technologies to reduce metal concentrations in effluent.

Understanding metal fate throughout wastewater treatment is important to identify removal pathways, as elimination from both soluble and particulate fractions may be necessary to comply with more stringent discharge quality requirements. Metals distributed in the particulate fraction are typically removed in conjunction with the elimination of TSS at WWTWs. Therefore, increasing HRT and SRT in primary and biological treatments may enhance metal removal rates. Nonetheless, changes to operating conditions often requires space for costly infrastructural developments, hence the application of alternative treatments may be preferred.

Soluble metal removal is highly variable and difficult to achieve in conventional wastewater treatment. Advances in particle size fractionation has allowed the soluble fraction to be separated into a colloidal fraction and a truly dissolved fraction, and metal distribution between these fractions is strongly influenced by the distribution of DOC. Nevertheless, the influence DOC has on metal fate is not well understood and the distribution of soluble metal species throughout wastewater treatment remains unexplored. It would, therefore, be beneficial to investigate these gaps in knowledge as they restrict our understanding of the mechanisms influencing metal fractionation, limiting the design and performance of suitable treatment processes to remove soluble as well as particulate metal from municipal wastewater.

Although many advanced technologies can be employed to treat wastewater laden with metals, it is important to note that initial metal concentration is a major factor to consider in the selection of the most suitable technique. Many studies have investigated the performance of treatment technologies, but only a small fraction have, however, investigated the capacity of techniques to remove metals from wastewater under actual municipal wastewater conditions. A review of these studies revealed that membrane filtration and adsorption by aquatic plants (in HFCWs) were the most frequently studied and applied processes. HFCWs have achieved removal rates over 80% for Cu, Pb and Zn. Barrier technologies such as NF and RO have achieved almost complete removal of investigated metals. It is, however, important to note that capital and operational costs (i.e. energy consumption, maintenance) as well as process simplicity, are key parameters that play a major role in the selection of suitable treatment systems. In most instances deployment of these technologies would be untenable, owing to the extremely high operating costs (i.e. energy consumption) of membrane treatment, and the requirement (and associated costs) of land space for HFCWs. Removal of metals to very low levels at acceptable financial and carbon cost is, therefore, likely to require the application of alternate techniques. Simpler, low-cost options such as coagulation-flocculation are available for metal removal. However, their capacity to remove metals under municipal wastewater conditions remains unexplored. This gap in knowledge hinders the design and application of suitable treatment technologies to enhance trace metal removal at municipal WWTWs, and contributes toward the unnecessary

application of expensive and carbon-intensive techniques. Thus, this is an area of research that requires investigation.

2.8 References

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Chapter 3

Distribution of Trace Metals (Cu, Pb, Ni, Zn) between Particulate, Colloidal and Truly Dissolved Fractions in Wastewater Treatment

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3. Distribution of Trace Metals (Cu, Pb, Ni, Zn) between Particulate, Colloidal and Truly Dissolved Fractions in Wastewater Treatment

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Abstract

The distribution of copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) between particulate, colloidal and truly dissolved size fractions in wastewater from a trickling filter treatment works was investigated. Samples of influent, primary effluent, humus effluent and final effluent were collected and separated into particulate (i.e. > 0.45 µm), colloidal (i.e. 1 kDa to 0.45 µm), and truly dissolved (i.e. < 1 kDa) fractions using membrane filters. In the influent, substantial proportions of Cu (60%), Pb (67%), and Zn (32%) were present in the particulate fraction which was removed in conjunction with suspended particles at the works in subsequent treatment stages. In final effluent, sizeable proportions of Cu (52%), Pb (32%), Ni (44%) and Zn (68%) were found within the colloidal size fraction. Calculated ratios of soluble metal to organic carbon suggest the metal to be adsorbed to or complexed with macromolecules typically found within the colloidal size range. These findings suggest that technologies capable of removing particles within the colloidal fraction have good potential to enhance metals removal from wastewater.

3.1 Introduction

Wastewater treatment works (WWTWs) receive metal inputs from both domestic and industrial sources, such that their discharges may cause harm in receiving waters (Stumm and Morgan, 2012). As a consequence of their potential to cause harm, there are regulatory drivers that require metals such as copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) to be removed as part of the wastewater treatment process. In the United States (US), the Clean Water Act (1972) defines Criteria Maximum Concentrations (CMC) and Criterion Continuous Concentrations (CCC) for heavy metals to protect aquatic life and human health in surface water. Hardness-based standards are currently used to assess compliance for Pb, Ni and Zn, however, since 2007 standards for Cu in the US have been determined using a Biotic Ligand Model (BLM), which uses site specific information on physico-chemical characteristics to convert a dissolved phase metal concentration into an equivalent bioavailable concentration (US Environmental Protection Agency [EPA], 2007). Within the European Union, the Water Framework Directive (WFD) (2000/60/EC) has recently specified bioavailability-based standards for Pb and Ni which are classified as Priority Hazardous Substances (PHS). In the United Kingdom (UK) bioavailability-based standards have also been specified for Cu and Zn (UK Technical Advisory Group [UKTAG], 2008), metals classified as Specific Pollutants under the WFD. Whilst improving the environmental relevance, bioavailability-based standards are, nonetheless, expected to significantly reduce acceptable metal concentrations in some instances (Peters et al. 2009). It is, however, difficult to reliably reduce trace metal concentrations in wastewater and studies have shown that removal rates at WWTWs vary considerably, regardless of the treatment/removal technology applied (Ziolko et al. 2011; Gardner et al. 2013).

The trickling filter treatment process is one of the oldest approaches used to treat wastewater, and, due to their low energy consumption and relative simplicity, is still the most common treatment process applied in small and medium sized WWTWs in the UK (Marquet et al. 2007). Hence, the ability to improve the metal removal performance of this treatment type will present a significant opportunity to reduce metal inputs to receiving waters. Trickling filter treatment involves dripping wastewater over media where microorganisms grow in a biofilm. Microorganisms produce and secrete extra-

cellular polymeric substances (EPS), which are high molecular weight polysaccharides and proteins with which metals can complex with (Pernet-coudrier et al. 2008; Sheng et al. 2013). Nevertheless, information about the behaviour of metals at trace level concentrations within the trickling filter process is scarce, possibly owing to difficulties in sampling the biomass. As such, the exact mechanism of metal removal by the biological film in trickling filters remains to be established (Ziolko et al. 2011). A study by Marquet et al. (2007), however, found that the performance of trickling filters was sensitive to the concentration of particles with a size between 1 and 50 μm . Such behaviour was linked to the proportion of colloidal material in the feed, thus gaining insight into the nature and size of particles throughout the wastewater treatment process could offer an opportunity to improve trickling filter performance with regard to metal removal.

Metals are traditionally considered to exist in two size fractions: a soluble fraction that passes through a filter with a pore size of 0.45 μm , and a particulate fraction which is retained on the filter (i.e. $> 0.45 \mu\text{m}$). Cu and Pb are known to have a high affinity for the particulate fraction and therefore can be removed via physical separation (Choubert et al. 2011). Conversely, Ni and Zn dominate in the soluble fraction, which is typically comprised of free metal ions, complexed metal, and metal entrained within colloidal suspensions (Worms et al. 2010a; Schijf and Zoll, 2011). In this case, adsorption, ion exchange or chemical modification processes are required for effective metal elimination (Martin et al. 1995).

Material within the soluble fraction can be separated into two further size fractions namely, a colloidal fraction, which encompasses material found in the size range 1 kDa to 0.45 μm , and a truly dissolved fraction, which is composed of constituents with a molecular weight $< 1 \text{ kDa}$ (Worms et al. 2010a). Metal distribution within the soluble fraction is influenced by the presence of functional groups (ligands) that may complex metal ions and, as such, the quantity and type of dissolved organic carbon (DOC) exerts an important influence on trace metal speciation (Ma et al. 2001). Whereas the concentration of DOC (usually in mg/L) quantifies the amount of organic matter present in wastewater the role of DOC in the behaviour of metals within effluent is not well

understood (Worms et al. 2010a). Furthermore, DOC is seldom measured in WWTWs (Katsoyiannis and Samara, 2007).

Studies on the characterisation of organic matter in effluent have found that the truly dissolved size fraction (< 1 kDa) is composed of amino acids, carbohydrates, vitamins, chlorophyll, synthetic ligands such as ethylenediaminetetraacetic acid (EDTA), and hydrated metal ions (Imai et al. 2002; Shon et al. 2006a). In contrast, organic matter in the colloidal size fraction (1 kDa to $0.45\ \mu\text{m}$) is predominantly composed of macromolecules including polysaccharides and proteins (Jarusutthirak et al. 2002; Nam and Amy, 2008) to which metals may adsorb or complex with in wastewater (Pernet-coudrier et al. 2008; Sheng et al. 2013). The presence of this colloidal material may confound traditional assumptions about how metals behave in solution (i.e. mechanisms other than complexation). Additionally, the lack of distinction between colloidal materials and other dissolved phase materials has limited the design and performance of wastewater treatment processes (Tchobanoglous et al. 2014).

Studies on the distribution of metals in WWTW effluents, those operating trickling filters in particular, are limited to conventional classification (i.e. soluble and particulate). Such simplified approach limits an understanding of those mechanisms influencing metal fractionation in wastewater. This is of particular importance as the removal of both soluble and particulate metal fractions during wastewater treatment may be necessary in order to comply with more stringent discharge quality requirements (Ziolko et al. 2011).

The aim of this study was to investigate the behaviour and fractionation of trace metals (Cu, Pb, Ni and Zn) in effluent from a works operating trickling filter treatment in order to better understand the potential options to enhance metal removal.

3.2 Materials and Methods

3.2.1 Study site

The effluent examined in this study was obtained from a WWTWs located in the UK which serves an urban catchment population (~22,000) treating, on average, $432,000\ \text{m}^3$ of influent per day. Contributors to the metal load entering the works include metals

corroded from the domestic water supply infrastructure, leaching of metal from household plumbing and inputs from diffuse sources, such as urban run-off. Influent is initially subject to screening and grit removal processes, followed by primary settling tanks and trickling filters. Tertiary treatment involves a nitrifying submerged aerated filter (NSAF), which has the function of removing ammonia, and DynaSand[®] filters which polish the effluent prior to discharge in the receiving water (Figure 3.1).

3.2.2 Sampling and analysis

Samples were collected over a 12-month period (February 2015 to January 2016) from a number of treatment stages at a trickling filter plant, namely; influent, primary effluent, humus effluent, final effluent and sludge holding tank (HT) returns (Figure 3.1). Grab samples of wastewater were taken at least once each month ($n = 14$). Grab samples of sludge HT returns were taken a minimum of every 4 months ($n = 3$). Samples were transported to, and were kept, in a refrigerated environment (4 °C) at Cranfield University laboratories.

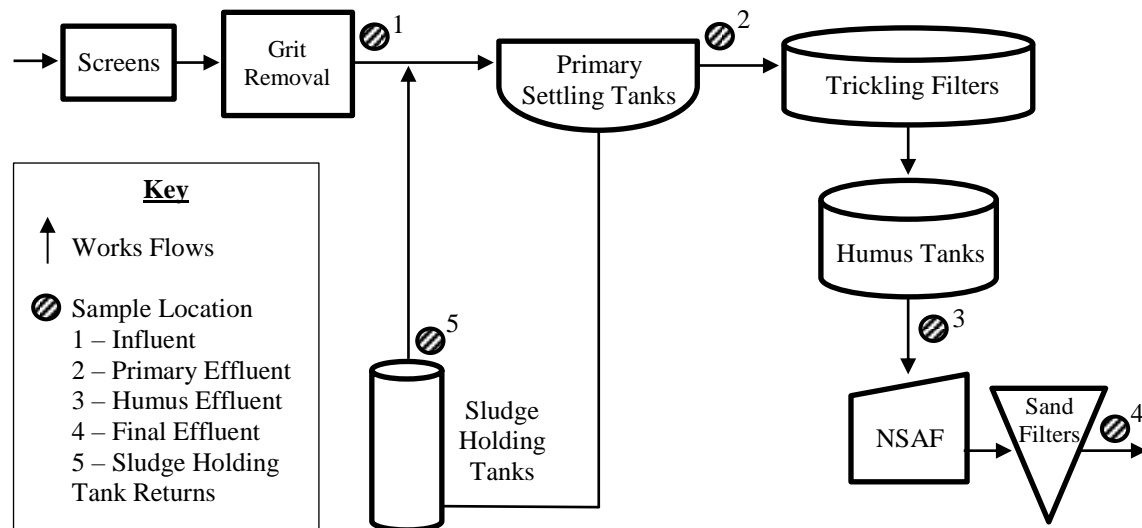


Figure 3.1 Simplified flow sheet for the site studied including sample locations.

Analysis of pH was conducted with a HANNA (HI 98120) probe (American Public Health Association [APHA], 2005). Total suspended solids (TSS) concentrations were obtained using standard vacuum filtration equipment (APHA, 2005). Total COD was determined by COD cell test kits (Fisher Scientific, Leicestershire, UK).

Particle size fractionation of the samples was conducted following a variation of the method described by Barker and Stuckey (1999). Initial fractionation of samples involved vacuum filtration (APHA, 2005) through 0.45 μm polyethersulphone membranes (Millipore, Livingston, UK) to obtain the soluble phase. Regenerated cellulose membranes (Millipore, Livingston, UK) were used to fractionate samples into low molar mass (LMM) colloidal (100 kDa) and so-called truly dissolved (1 kDa) phases. All membranes were washed in sequences of ultrapure water (0.05 μS conductivity level), 0.01 M sodium hydroxide (NaOH) (reagent grade, Fisher Scientific, Loughborough, UK) and 0.01 M hydrochloric acid (HCl) (reagent grade, Fisher Scientific, Loughborough, UK). This alkaline/acid cleaning sequence was repeated after each use; subsequently the membranes were stored in a 10 % ethanol solution (reagent grade, Sigma-aldrich, Gillingham, UK). The LMM colloidal and truly dissolved fractions were obtained by operating an Amicon 8400 stirred pressure cell (Millipore, Livingston, UK). Filtration was driven by nitrogen gas at a pressure of 20 kPa for 100 kDa membranes and 160 kPa for 1 kDa membranes. In all instances, samples were filtered progressively through the series of membranes. The membrane cell was stored in a 2% nitric acid (HNO_3) bath (reagent grade, Fisher Scientific, Loughborough, UK) between uses and all plastic and glassware were alkaline and acid washed before being stored in 2% HNO_3 . To limit concentration polarisation of solute at the membrane surface, an integrated bar stirrer was operated and a filtrate/retentate ratio of 0.4 was adopted.

Fractionated samples were analysed for DOC with a TOC-V analyser (Shimadzu, Milton Keynes, UK). Target metals (Cu, Pb, Ni and Zn) were measured with an ELAN 9000 inductively coupled plasma-mass spectrometer (ICP-MS) (Perkin Elmer, Beaconsfield, UK). The limit of detection for all the metals was 0.01 $\mu\text{g/L}$. Certified calibration standards were used to check analytical accuracy. Both calibration solutions and samples were spiked with rhodium which was used as an internal standard. As membranes may introduce background contribution of the target metals, sample blanks were processed through the filtration and ultrafiltration procedures. Metal concentrations in the sample blanks were subtracted from those measured in the corresponding permeates. To determine the total concentration of each target metal by ICP-MS, unfiltered samples were digested with a CEM-MARS microwave (CEM,

Buckingham, UK). Phase distributions were calculated as follows: particulate = total - soluble, high molar mass (HMM) colloidal = soluble - LMM colloidal, LMM colloidal = LMM colloidal - truly dissolved.

Statistical analysis of the obtained data was done with the software package Minitab 17. One- way ANOVA tests were performed to assess the differences in metal presence and phase distribution between samples. Pearson's correlation coefficient tests were used to identify relationships between the concentration of metals and total suspended solids (TSS). Correlation strength was determined to be weak (0.2-0.39), moderate (0.4-0.59) or strong (> 0.59) using guidance from Evans (1996). Both tests were conducted with a level of significance $p < 0.05$.

3.3. Results and discussion

3.3.1 Works performance

The concentrations and rates of removal found across different treatment stages for the considered determinands are summarised in Table 3.1. The overall rates of removal for TSS (95%) and COD (86%) indicated that operating conditions at the site were typical and in line with expectations for treatment works of this type (Table 3.1). Influent and final effluent concentrations of these determinands were also within the range reported for trickling filter works in the UK (Gardner et al. 2013).

At the works, limited DOC elimination was observed in primary treatment (16%) since this stage is responsible for the removal of particulate matter. During secondary treatment a 48% DOC removal was, however, within the range (40-66%) reported by Confer et al. (1995) for a works operating trickling filter treatment. Discharge concentrations were also comparable to values reported for other WWTWs (Shafer et al. 1998).

The abundance of target metals in terms of total concentration followed the order $Zn > Cu > Ni > Pb$ (see Table 3.1). The concentrations of trace metals found in the influent were similar to those reported by other investigators at WWTWs elsewhere (Table 3.2). Additionally, final effluent metal concentrations were comparable to values reported in other UK studies (Gardner et al. 2013).

Table 3.1 Concentrations and rates of removal observed for sanitary determinands and metals at the site studied [Mean \pm standard deviation (SD)].

Parameter	Influent	Primary Effluent	Humus Effluent	Final Effluent	Primary Removal (%)	Secondary Removal (%)	Tertiary Removal (%)	Overall Removal (%)
TSS (mg/L)	205 (68)	84 (47)	28 (13)	9 (4)	57 (11)	63 (15)	61 (21)	95 (3)
COD (mg/L)	644 (303)	244 (118)	110 (62)	80 (40)	61 (12)	54 (19)	32 (18)	86 (7)
DOC (mg/L)	34 (10)	29 (10)	14 (7)	9 (8)	16 (14)	48 (25)	44 (26)	75 (19)
pH	8.1 (0.4)	8 (0.3)	7.8 (0.2)	7.4 (0.2)	-	-	-	-
Cu ($\mu\text{g/L}$)	51 (25)	39 (18)	25 (8)	18 (6)	22 (11)	32 (19)	35 (15)	60 (19)
Pb ($\mu\text{g/L}$)	4 (2)	3 (2)	2 (1)	1.2 (0.8)	23 (17)	36 (19)	37 (27)	58 (24)
Ni ($\mu\text{g/L}$)	13 (7)	12 (7)	10 (5)	10 (5)	22 (11)	16 (10)	1 (25)	28 (12)
Zn ($\mu\text{g/L}$)	115 (36)	96 (26)	76 (20)	56 (8)	20 (9)	22 (19)	22 (21)	47 (17)

Table 3.2 Influent metal concentrations ($\mu\text{g/L}$) at WWTWs worldwide compared with those observed at the site studied (Mean).

Location	Cu	Pb	Ni	Zn	Reference
Nancy, France	59	6	7	140	Houhou et al. 2009
Study of 30 different WWTPs, UK	78	25	14	155	Rule et al. 2006
Milwaukee, US	73	11	11	164	Soonthornnonda and Christensen, 2008
Study of 16 different WWTPs, UK	76	17	14	180	Gardner et al. 2013
Site studied, UK	51	4	13	115	Hargreaves et al. 2017

3.3.2 Whole works effect on the phase distribution of metals in wastewater

The metal concentrations observed in the LMM colloidal and HMM colloidal fractions showed a high level of variability, such that, no statistically significant differences between these fractions could be detected (one-way ANOVA, $p > 0.05$). Consequently, these fractions were combined into a single colloidal size fraction (from 0.45 μm to 1 kDa). The distribution of target metals within the particulate, colloidal and truly dissolved fractions at different treatment stages are presented in Figure 3.2.

3.3.2.1 Copper and lead

Good overall rates of removal were observed for Cu (60%) and Pb (58%) at the site studied (Table 3.1). For the particulate fraction in particular, a high level of removal occurred as indicated by significantly lower concentrations of Cu ($p < 0.001$) and Pb ($p < 0.001$) found in the final effluent (Table 3.1). Strong correlations were observed between TSS and particulate phase metal concentrations for Cu ($r = 0.732$, $p < 0.001$) and Pb ($r = 0.727$, $p < 0.001$), which indicate that removal of both metals occurred in conjunction with the elimination of suspended particles. The proportion of Cu and Pb in the particulate fraction in the influent and the overall rate of removal that was observed was similar to that found in other studies (Shafer et al. 1998; Karvelas et al. 2003).

Appreciable amounts of Cu (28%) and Pb (27%) were found in the colloidal fraction of the influent (Figure 3.2a). Although colloidal removal for these metals was significant, as p values were 0.001 and less than 0.001 for Cu and Pb respectively, residual concentrations of Cu (8.8 $\mu\text{g/L}$) and Pb (0.3 $\mu\text{g/L}$) remained in the colloidal fraction following treatment (see Figure 3.2d). This finding was in line with expectation, as soluble Cu and Pb typically adsorb onto the surface of colloidal materials (Martin et al. 1995). Furthermore, other studies have shown a large proportion of Cu to exist within similar colloidal size fractions in final effluent. For example, Shafer et al. (1998) observed 30% distribution of Cu within the size fraction 10 kDa to 0.22 μm . Worms et al. (2010a) found substantial proportions of Cu and Pb in the colloidal size fraction (0.45 μm -1 kDa) and reported that the distribution of metals between colloidal and truly dissolved fractions was strongly influenced by the distribution of DOC within these same fractions.

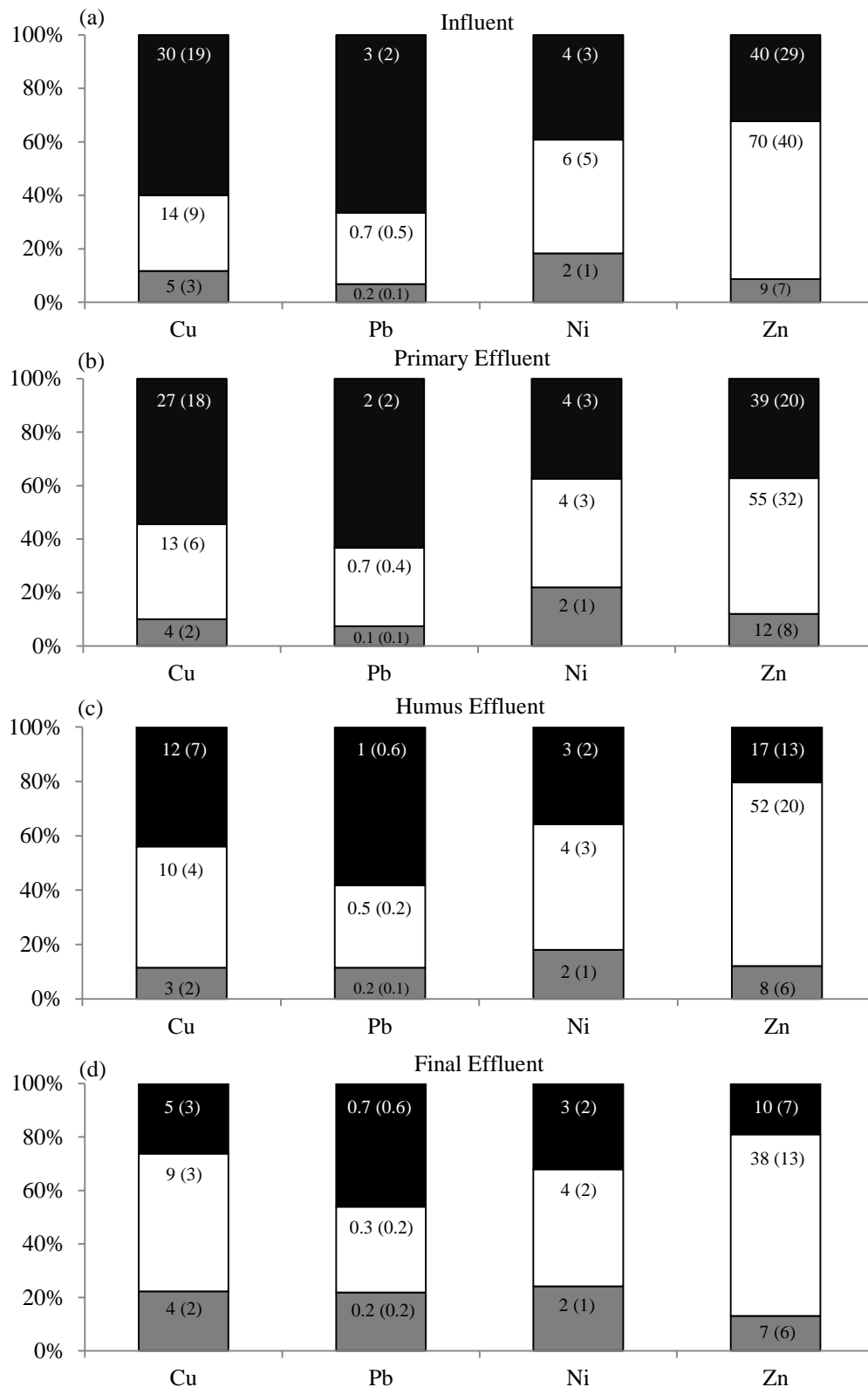


Figure 3.2 Distribution of metals in particulate (black), colloidal (white) and truly dissolved (grey) fractions in influent (a), primary effluent (b), humus effluent (c) and final effluent (d) at the site studied. Values shown are metal concentrations ($\mu\text{g/L}$) in each size fraction (Mean \pm SD).

DOC is composed of organic compounds with functional groups (ligands) that have a high affinity for metal ions (Sarathy and Allen, 2005; Constantino et al. 2015). The distribution of DOC within wastewater at the site studied (see Figure 3.3) was greater in the colloidal fraction compared with the truly dissolved fraction, as found in effluents elsewhere (Worms et al. 2010b). To compare the relative affinity of the target metals for organic ligands in the soluble fraction, the molar ratios of metals to organic carbon were calculated in final effluent at the site (see Table 3.3). This analysis found that the proportions of Cu (79%) and Pb (71%) were highest in the colloidal fraction. Other studies have found that the colloidal size fraction is predominantly composed of macromolecules, such as polysaccharides and proteins, to which metals can adsorb to or complex with (Jarusutthirak et al. 2002; Nam and Amy, 2008; Sheng et al. 2013). Hence, the findings from the present study suggest that a sizeable proportion of Cu and Pb may be adsorbed to or complexed with macromolecules present in the colloidal size fraction.

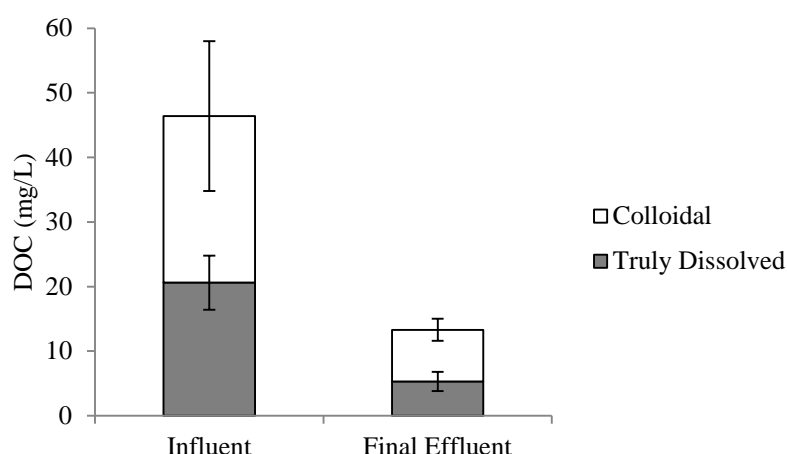


Figure 3.3 DOC concentrations in colloidal (white) and truly dissolved (grey) size fractions in influent and final effluent at the site studied (Mean \pm SD).

Compared with particulate and colloidal fractions, a relatively small proportion of Cu (12%) and Pb (7%) were observed in the truly dissolved size fraction of the influent (Figure 3.2a). For Pb, no statistically significant difference was observed between influent and final effluent ($p = 0.082$). Truly dissolved Cu concentrations were significantly lower in final effluent ($p = 0.026$), although Cu removal from this fraction was negligible (2%). This suggests that the treatment technologies operating at the works had little or no effect on Cu and Pb found within this fraction (Figure 3.2d). In

fact, other studies (Imai et al. 2002; Shon et al. 2006a) have identified that the truly dissolved fraction in wastewater comprises free metal ions, organic constituents, including amino acids, carbohydrates, and synthetic ligands (such as EDTA), and inorganic components (including sulphur, nitrogen, chlorides) which metals may adsorb too and/or complex with. These constituents are known to be resistant to removal so that negligible removals for metals associated to them can be expected.

Table 3.3 Soluble phase metals to organic carbon molar ratios and their relative proportions in final effluent at the works (Mean).

Metal / DOC ($\mu\text{mmetal} / \text{mmolC}$)	Cu	Pb	Ni	Zn
Truly Dissolved	0.101 (21%)	0.002 (29%)	0.055 (36%)	0.398 (26%)
Colloidal	0.379 (79%)	0.005 (71%)	0.100 (64%)	1.147 (74%)

3.3.2.2 Nickel and zinc

As shown in Figure 3.2a, Ni and Zn were predominantly found in the colloidal fraction of the influent with sizeable proportions in particulate form, this is, 39% for Ni and 32% for Zn. Additionally, small amounts of Ni (18%) and Zn (9%) were observed in the truly dissolved phase.

A low overall rate of removal (28%) was observed for Ni (see Table 3.1), with no significant correlation identified between particulate Ni and TSS concentrations ($r = 0.222$, $p = 0.101$). This metal is highly soluble and, because of its low affinity for suspended matter (Karvelas et al. 2003), its removal during wastewater treatment is low (Schafer et al. 1998), especially when compared with Cu, Pb and Zn (see Table 3.1). Although particulate Ni concentrations were significantly lower in the final effluent ($p = 0.012$), only a small amount of Ni (29%) was removed from this fraction. In addition, Ni concentrations measured in the colloidal ($p = 0.073$) and truly dissolved ($p = 0.727$) fractions were not significantly different from those observed in the influent. These findings indicate that Ni persists after treatment with little or no change in its distribution between particle size fractions (see Figure 3.2d). Such behaviour was

expected as other studies reported similar findings at WWTWs elsewhere (Karvelas et al. 2003).

Approximately half of the initial Zn load was removed at the site (Table 3.1). A moderate correlation was observed between particulate phase Zn and TSS concentrations ($r = 0.480$, $p < 0.001$) with a significantly lower Zn concentration ($p < 0.001$) observed in the particulate fraction of final effluent. These findings indicate that Zn, albeit to a lesser degree than Cu and Pb, has some affinity for suspended particles in wastewater as reported by Karvelas et al. (2003). Elimination of Zn from the particulate fraction was accompanied by removal, to a lesser degree, from the colloidal fraction. As such, an increase in the ratio of colloidal to particulate Zn was observed in final effluent (see Figure 3.2d). In the truly dissolved fraction no significant change ($p = 0.060$) was measured, thus indicating that Zn in the truly dissolved fraction remained as for Cu, Pb and Ni.

Residual amounts of Zn as well as Ni were predominantly found in the colloidal size fraction of the final effluent (see Figure 3.2d). This was unexpected since Ni and Zn are highly soluble in wastewater and, given what is understood of their thermodynamic properties (i.e. slow rate of reaction, low stability constants), a large proportion of soluble Ni and Zn was expected to remain unbound in the free ionic form and distributed within the truly dissolved size fraction. Worms et al. (2010) reported, however, that Ni and Zn can interact with colloidal organic materials in the colloidal size fraction (0.45 μm -1 kDa). At the site studied, calculated molar ratios of soluble metals to organic carbon indicate that dissolved species in the colloidal size range are relevant for the binding of Ni and Zn (see Table 3.2). Compared with other target metals, more Ni (36%) was found in the truly dissolved fraction although, similar to Cu and Pb, the highest relative proportions of Ni (64%) and Zn (74%) were found in the colloidal fraction (Table 3.2). This indicates that Ni and Zn may also be adsorbed to or complexed with macromolecules present in the colloidal size range. It is therefore plausible that removing organic materials within the colloidal size fraction could present an opportunity to reduce the concentrations of all target metals (Cu, Pb, Ni and Zn) in effluent discharges.

3.3.3 Effect of treatment stages on the phase distribution of metals in wastewater

3.3.3.1 Primary treatment

Comparable removal rates for Cu, Pb, Ni and Zn were found in the primary settling tank at the site studied (see Table 3.1). In particular, removal of Cu (36%), Pb (30%), Ni (31%) and Zn (28%) occurred from the particulate fraction. These findings indicate that, when present in particulate form, metals readily settle during primary treatment, hence the comparable removal rates observed for Cu, Pb, Ni and Zn regardless of the fraction (suspended or soluble) in which metals were predominantly found. Similar results were reported by Karvelas et al. (2003) who also found that the distribution of soluble to particulate metal increased in primary effluent as herein shown in Figure 3.2 for Cu, Pb and Ni.

3.3.3.2 Secondary treatment

Good removals for Cu (32%) and Pb (36%) were achieved at the secondary treatment stage. In particular, substantial elimination of Cu (54%) and Pb (51%) from the particulate fraction was observed. Given that the trickling filter effectively removed TSS (63%) and that, when in particulate form, Cu and Pb were removed in conjunction with suspended particles, such results were anticipated.

Despite the removal of particulate Cu and Pb, only a small reduction in the proportion of these metals in the particulate fraction of humus effluent was observed (see Figure 3.2c). This occurred as Cu (36%) and Pb (27%) were also removed from the soluble fraction at the secondary treatment stage. Within biological treatment, biomass produces and secretes EPS, a mixture of high molecular weight polysaccharides and proteins that can act as strong ligands for metals (Sheng et al. 2013). The strong affinity Cu and Pb have for EPS means these metals can dissociate readily from soluble complexes to undergo removal in association with biomass (Sheng et al. 2013).

Unlike Cu and Pb, no significant change in soluble concentrations of Ni or Zn was observed, owing to the lower affinity these metals have for EPS (Savvaidis et al. 2003; Comte et al. 2006), thus accounting for the comparably lower removal rates trickling filter treatment achieved for Ni and Zn (see Table 3.1). In fact, during biological treatments direct settling is suggested to be of greater significance for the removal of Ni

and Zn (Stephenson and Lester, 1987). This was the case for Zn at the works studied with significantly lower particulate phase Zn ($p < 0.001$) concentrations measured in humus effluent, accounting for the good rate of removal (38%) from this fraction. Trickling filter treatment did, however, have no statistically significant influence on particulate phase Ni concentrations ($p = 0.92$).

3.3.3.3 Tertiary treatment

Good rates of removal were observed for Cu (35%) and Pb (37%) at the tertiary treatment stage, whilst a relatively moderate removal extent was measured for Zn (22%). In the particulate and colloidal fractions of final effluent significant decreases in the concentrations of Cu, Pb and Zn were observed. These findings were in line with expectation as, similar to primary and secondary treatment, a good rate of TSS removal (61%) was achieved, enabling removal of particulate metal in conjunction with suspended particles at the tertiary treatment stage. Furthermore, other studies (Mostafa and Aly, 2013) have identified that Dynasand[®] filters instigate the removal of particles by flocculation. This process encourages the agglomeration of colloidal materials, which metals may be adsorbed to or complexed with, into larger aggregates that are retained on the filter.

For Cu and Pb, decreases in concentrations of particulate and colloidal phase metal corresponded with an increase (12 to 22%) in truly dissolved distribution in final effluent (Figure 3d). This finding was supported by significant increases in metal concentrations when comparing the truly dissolved fraction in humus effluent and final effluent samples for Cu ($p = 0.008$) and Pb ($p = 0.032$), indicating that release of these metals was occurring within tertiary treatment.

As the concentration of organics in the colloidal size fraction decreased from 12.4 to 8 mg/L, the DOC concentration within the truly dissolved phase increased from 3.5 to 5.3 mg/L. Since a substantial proportion of Cu (45%) and Pb (30%) was observed within the colloidal size fraction in humus effluent (Figure 3.2c), the concentration of these metals increase in the final effluent as suspended/colloidal organics become truly dissolved. Thus, suggesting that the release of metals was influenced by DOC removal in the tertiary treatment stage.

Nevertheless, the relationship between metals and DOC release reflects only a weak correlation for both Cu ($r = 0.299$) and Pb ($r = 0.254$), which suggests that DOC is not the only contributing parameter toward metal release observed. The NSAF process, included as part of tertiary treatment at the works (Figure 3.1), could also contribute to metal release. In this process alkalinity consumption, owing to nitrification, lowers pH so that the presence of protons reduces the stability of metal complexes and enhances metal concentrations in the truly dissolved fraction.

A negligible overall rate of removal (1%) was recorded for Ni at the tertiary treatment stage (Table 3.1). In addition, little change was observed in the distribution of Ni between particle size fractions (see Figure 3.2d), indicating that processes operated as part of tertiary treatment at the studied works had little effect on Ni.

3.3.4 Phase distribution of metals in sewage sludge

Within sludge returns, a proportion of each metal was observed within the particulate fraction, with Cu and Pb showing larger distributions when compared with Ni and Zn (Figure 3.4). This occurs as Cu and Pb have a high affinity for particulate organic matter in sewage sludge (García-Delgado et al. 2007). The greater abundance of Ni and Zn in the soluble fraction indicates that these metals have higher mobility within sludge, as reported by Ščančar et al. (2000). However, despite differing mobility, a similar distribution was found for Cu, Pb and Zn in the colloidal size fraction within sludge HT returns (Figure 3.4). Sludge returns are expected to contain organic colloids with which metals can bind (Buzier et al. 2006) and metal complexation with soluble organic matter in sewage sludge has been reported elsewhere (Stylianou et al. 2007). In the presence of high divalent cation concentrations, such as those observed herein for Cu (143.1 µg/L), Pb (8.4 µg/L), Ni (38.4 µg/L) and Zn (223.5 µg/L), the structure of organic matter can change from a stretched linear configuration to a coiled and compact arrangement (Shon et al. 2006b). These structural alterations are thought to increase the availability of colloidal material owing to the formation of protein-like aggregates that metals can adsorb to and/or complex with (Guibaud et al. 2003). Hence explaining why target metals were predominately found in the colloidal size fraction of the sludge returns (Figure 3.4).

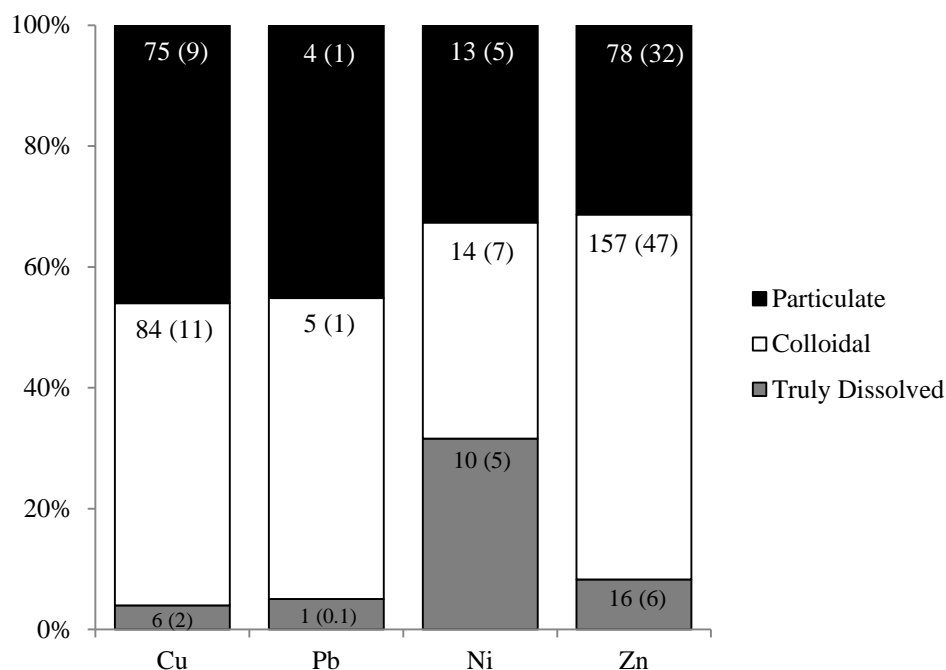


Figure 3.4 Distribution of metals in particulate (black), colloidal (white) and truly dissolved (grey) phases in sludge HT returns at the site studied. Values shown are metal concentrations ($\mu\text{g/L}$) in each size fraction (Mean \pm SD).

The relatively high proportion of Ni within the truly dissolved fraction compared with other metals studied (Figure 3.4) has also been observed elsewhere (Ščančar et al. 2000). This occurs due to the higher selectivity of polyanions towards metals such as Cu for the formation of metal complexes, which in turn blocks functional groups (Ščančar et al. 2000). Blocking of functional groups has been found to reduce binding of Ni to a much greater extent than other metals so that a high proportion of this metal remains in the free ionic form (da Costa Cunha et al. 2015).

3.4 Conclusions

The experimental findings herein presented support the concept that particle size fractionation in wastewater helps to understand potential treatment options to enhance metal removal.

In sewage influent, Cu and Pb were predominantly observed in the particulate fraction. Removal from this fraction in subsequent treatment stages was strongly dependant on TSS elimination. During treatment, a sizable proportion of Zn in the influent was also found in the particulate fraction and showed moderate interaction with suspended

particles; thus Zn and TSS removals were interdependent, albeit to a lesser degree than Cu and Pb. Because of a weak interaction with suspended particles, the overall rate of removal for Ni was not affected by TSS removal at the works.

After treatment, a substantial proportion of the residual Cu, Pb, Ni and Zn were found in the colloidal fraction of the final effluent. Calculated ratios of soluble metal to organic carbon in the final effluent determined that species in the colloidal size range had an important role in the binding of target metals. Such finding indicates that Cu, Pb, Ni and Zn may be adsorbed to or complexed with macromolecules (e.g. proteins, polysaccharides) typically present in the colloidal size fraction. Results from the present study therefore suggest that technologies capable of removing particles within the colloidal size fraction could also reduce the concentrations of Cu, Pb, Ni and Zn in final effluent discharges.

Relative to colloidal and particulate fractions, only a small concentration of Cu, Pb, Ni and Zn was found in the truly dissolved fraction of influent and was not statistically different in final effluent. Hence treatment technologies operating at the studied works had little or no effect on metal found within the truly dissolved fraction.

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Chapter 4

Coagulation-flocculation Process with Metal Salts, Synthetic Polymers and Biopolymers for the Removal of Trace Metals (Cu, Pb, Ni, Zn) from Municipal Wastewater

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4. Coagulation-flocculation Process with Metal Salts, Synthetic Polymers and Biopolymers for the Removal of Trace Metals (Cu, Pb, Ni, Zn) from Municipal Wastewater

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Abstract

To ensure compliance with regulatory standards, it is important to examine the potential of treatment technologies to enhance trace metal removal from wastewater. This study investigated the effectiveness of coagulation-flocculation at removing trace metals from humus effluent with ferric chloride (FeCl_3), the synthetic polymer polyethyleneimine (PEI), and the biopolymers chitosan and Flocculan. Effluent samples were collected from a trickling filter treatment works operating in the United Kingdom and contained 21 ± 4 $\mu\text{g/L}$ copper (Cu), 0.8 ± 0.1 $\mu\text{g/L}$ lead (Pb), 4 ± 1 $\mu\text{g/L}$ nickel (Ni) and 43 ± 9 $\mu\text{g/L}$ zinc (Zn). The influence of coagulant dosage and the velocity and time of the slow mixing stage were studied via a series of jar tests. Chitosan and PEI had a moderate effect on the removal of trace metals ($\leq 35\%$). FeCl_3 removed 48% Cu, 56% Pb and 41% Zn at the optimised dose of 0.10 mg/L. At the optimised dose of 0.25 mg/L, Flocculan removed 77% Cu, 68% Pb and 42% Zn. The dominant mechanism for particle removal by FeCl_3 was enmeshment in the precipitates (i.e. sweep flocculation) whereas, for Flocculan, inter-particle bridging was the dominant removal mechanism. Overall, FeCl_3 and Flocculan were found to be most effective at removing trace metals from wastewater.

4.1. Introduction

Metals such as copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) are frequently present in municipal wastewater at concentrations in the $\mu\text{g/L}$ range. As a consequence of their potential to cause harm (Jaishankar et al. 2014), regulatory drivers require the mentioned metals to be removed during wastewater treatment. For example, in the United States (US), the Clean Water Act (1972) defines Criteria Maximum Concentrations (CMC) and Criterion Continuous Concentrations (CCC) for heavy metals to protect aquatic life and human health in surface water. In the European Union, the Water Framework Directive (WFD) (2000/60/EC) has recently specified bioavailability-based standards for Pb and Ni which are classified as Priority Hazardous Substances. Bioavailability-based standards have also been specified for Cu and Zn, classified as Specific Pollutants under the WFD, in the United Kingdom (UK) (UK Technical Advisory Group [UKTAG], 2008). Bioavailable metal concentrations are calculated using a biotic ligand model (BLM). This model converts a dissolved phase metal concentration into an equivalent bioavailable concentration by considering specific information on physico-chemical characteristics such as pH, water hardness, and the concentration of dissolved organic carbon (DOC) (Di Toro et al. 2001). Whilst improving the environmental relevance, bioavailability-based standards are expected to significantly reduce acceptable metal concentrations in treated effluents (Peters et al. 2009). It is, however, difficult to reduce trace metal concentrations in wastewater and studies have shown that rates of removal vary considerably at wastewater treatment works (WWTWs) (Ziolko et al. 2011; Gardner et al. 2013). Faced with the expectation of more stringent regulation, many advanced treatment technologies are being operated for the removal of heavy metal ions from wastewater. Technologies include chemical precipitation, membrane filtration, adsorption, or ion-exchange. Issues have, however, been denoted with technologies in many instances found to be expensive and inadequate to achieve final effluent requirements (Chapter 2).

Metal fractionation in wastewater is an important consideration when choosing potential options to enhance metal removal. Traditionally, metals are considered to exist in two fractions: a soluble fraction that passes through a filter with a pore size of $0.45\ \mu\text{m}$, and a particulate fraction which is retained on the filter (i.e. $> 0.45\ \mu\text{m}$). At WWTWs, Cu

and Pb are known to have a high affinity for the particulate fraction (Karvelas et al. 2003; Buzier et al. 2006) and, thus, can be removed by physical separation (Choubert et al. 2011). Conversely, Ni and Zn abound in the soluble fraction, which requires adsorption, ion exchange or chemical modification for their effective elimination (Martin et al. 1995). Such two-fraction distinction has been challenged by recent findings (Worms et al. 2010; Hargreaves et al. 2017) that indicate metals can adsorb or complex with organic material within the colloidal size fraction (1 kDa - 0.45 μ m). Such findings suggest that technologies capable of removing particles within the colloidal fraction have good potential to enhance metals removal from wastewater (Hargreaves et al. 2017).

One such technology is coagulation-flocculation (CF), a frequently applied process in the treatment of drinking water and the purification of industrial effluents. Coagulation with chemical coagulants involves combining insoluble particles and dissolved organic matter into larger aggregates which can be removed in subsequent sedimentation and filtration stages (Renault et al. 2009). Coagulants destabilise suspended and colloidal particles in wastewater by forming micro-flocs. These are aggregated by flocculation, which consists of a stirring/agitation procedure that encourages particles to clump allowing their removal in subsequent treatment stages (Tchobanoglous et al. 2014). Mechanisms through which particles and colloids are aggregated and, thus, removed can involve a combination of charge neutralisation, adsorption, entrapment and complexation processes (Alexander et al. 2012).

Coagulants frequently used include inorganic salts such as ferric chloride (FeCl_3) or synthetic polymers such as polyethyleneimine (PEI). FeCl_3 has been utilised to enhance the removal of Cu, Pb, Ni and Zn from synthetic wastewater (Johnson et al. 2008) and aggregates particles by charge neutralisation and sweep flocculation (Duan and Gregory, 2003). Charge neutralisation refers to the sorption of two particles with opposite charged ions, whereas sweep flocculation entails the enmeshment of particles in a growing hydroxide precipitate. Synthetic polymers agglomerate particles by inter-particle bridging. This phenomenon involves the sorption of particles onto polymeric chains by forming particle-polymer-particle complexes (Shak and Wu, 2014). The loops and tails of adsorbed polymeric chains can protrude and attach to other particles in the

medium, allowing bridging of particles to occur (Shak and Wu, 2014). Synthetic polymers have also shown the ability to enhance metals removal. When it comes to the application of these products, a limited number of studies have reported on the removal of metal from municipal wastewater.

The use of metal salts and synthetic polymers may have consequences that are detrimental to the environment such as increasing non-target metal concentrations in treated wastewater, the production of large volumes of sludge, and significant alterations to pH of treated wastewater (Renault et al. 2009; Vijayaraghavan et al. 2011). For these reasons, alternative reagents have been considered for CF treatment. Biopolymers such as chitosan and Flocculant are of great interest since they are natural low-cost products with environmentally friendly characteristics such as biodegradability, no toxicity and produced from a renewable resource (Renault et al. 2009). Chitosan is obtained from the alkaline deacetylation of chitin, a biopolymer extracted from shellfish sources, and possesses intrinsic properties including high cationic charge density and long polymer chains and, thus, has been applied in the treatment of different effluents (Renault et al. 2009). Flocculant is an aqueous solution composed of up to 30% Tanfloc. Obtained from *Acacia mearnsii* bark, Tanfloc is a tannin-based product modified to include a quaternary nitrogen which provides a cationic character (Beltrán Heredia and Sánchez Martín, 2009). Studies have identified that Tanfloc can enhance the removal of metals from polluted surface water (Beltrán Heredia and Sánchez Martín, 2009). Nevertheless, investigations into the application of the more commercially available Flocculant for the treatment of wastewater are limited. Furthermore, it is noted that there is a scarcity of comprehensive studies that compare the effectiveness of natural coagulants, synthetic polymers and conventional coagulants. This gap in knowledge may hinder their potential for application to enhance trace metal removal at WWTWs. The aim of this study was, therefore, to compare the metal removal performance of the biopolymers chitosan and Flocculant with that of the conventional coagulant, FeCl_3 , and the synthetic polymer, PEI.

4.2 Materials and Methods

4.2.1 Wastewater samples

Coagulation-flocculation experiments were conducted with humus effluent for two reasons, namely, the amount of reagent required for coagulation is lower than that needed with primary effluent so that sludge production is minimized. Secondly, if dosed at this point the sludge generated can be removed in a subsequent sand filtration operated on site as part of the tertiary treatment. Humus effluent samples were collected from a full scale WWTWs operating trickling filters in the UK. Samples ($n = 6$) were taken at least once each month over a 5-month study period (from May to September 2016). Samples were collected in 20 L plastic containers and were transported to, and were kept, in a refrigerated environment ($4\text{ }^{\circ}\text{C}$) at Cranfield University laboratories.

4.2.2 Coagulants

The PEI was received as a 50% by weight solution from Sigma-Aldrich (Gillingham, UK). This was the branched chain form of the polymer with an average molecular weight of 750,000 Da (Cat No: 181978). A PEI stock solution (1 g/L) was prepared with deionised water. Chitosan powder, derived from shrimp shells (practical grade, Cat No: 417963), was also obtained from Sigma-Aldrich. A chitosan stock solution (500 mg/L) was prepared as described by Rizzo et al. (2008). Briefly, 100 mg of chitosan powder was dissolved in 0.5 mL of 2 M hydrochloric acid solution (reagent grade, Fisher Scientific, Loughborough, UK) and 9.5 mL of deionised water; after 60 min, 190 mL of deionised water was added. A FeCl_3 solution (40%) was obtained from Darrant Chemicals (Lincoln, UK). Flocculant solution was obtained from Lansdowne Chemicals (Oxon, UK).

4.2.3 Coagulation-flocculation experiments

The CF studies were conducted in a conventional jar test apparatus (Phipps and Bird, Richmond, United States), which allowed six beakers to be agitated simultaneously. Each jar test consisted of a batch experiment involving rapid mixing, slow mixing and sedimentation. Plastic beakers were filled with 1 L of humus effluent, placed on the floc illuminator and once coagulant dosage was added, agitated at the preselected intensity of rapid mixing (100 RPM for 2 min). Once the rapid mixing was complete, the preselected intensity of slow mixing (40 RPM for 30 min) was immediately established. After slow mixing, beakers were removed from the floc illuminator for a 30 min

sedimentation phase to take place. Subsequently, supernatant was withdrawn from about 25 mm below the surface with a syringe.

Preliminary jar tests investigating a wide range of doses (0.25 to 8 mg/L for FeCl_3 , 0.25 to 40 mg/L for Flocculan, chitosan and PEI, and 0.10 to 2 g/L for PEI in 50% by weight solution) were carried out to identify if the reagents were capable of achieving the desired metal removal, this is, over 35% for at least two of the tested metals (Cu, Pb, Ni, Zn). Coagulants not capable of achieving this condition were eliminated from subsequent experiments for optimisation of coagulant dose and slow mixing conditions. In order to optimise coagulant dose narrow ranges of dose were selected for further investigation: 0.05 to 0.40 mg/L for FeCl_3 and 0.10 to 2 mg/L for Flocculan. In optimising coagulant dose, one beaker in each run had no coagulant added to it and was therefore treated by stirring only. This was used as the experimental control.

To identify the optimum slow mixing conditions, both agitation time and speed were assessed. In these experiments, the established optimum coagulant dose for either FeCl_3 (0.10 mg/L) or Flocculan (0.25 mg/L) was added to the jars and rapid mixing conditions (100 rpm for 2 min) remained constant. The slow mixing intensity was investigated in the range 0-50 rpm with a fixed agitation time of 30 min, whilst the duration of slow mixing was investigated in the range 0-50 min with a fixed agitation speed of 40 rpm. A beaker agitated by rapid mixing only was used as the experimental control.

4.2.4 Chemical analysis

Prior to inductively coupled plasma-mass spectrometer (ICP-MS) analysis, samples were digested with nitric acid (reagent grade, Fisher Scientific, Loughborough, UK) in a CEM-MARS microwave (CEM, Buckingham, UK). Certified calibration standards were used to check analytical accuracy. The limit of detection for all the metals was 0.01 $\mu\text{g/L}$. Both calibration solutions and sample extracts were spiked with a four mixed elements solution (containing selenium, germanium, rhodium, bismuth) for internal standardisation across the full mass range. A Jenway 4330 pH and conductivity meter (Stone, UK) was used for pH measurement. Turbidity was determined with a HACH 2100N turbidimeter (Manchester, UK). Total chemical oxygen demand (COD) and total phosphorous (TP) concentrations were determined with cell test kits (Fisher Scientific,

Leicestershire, UK). After vacuum filtration (APHA, 2005) through 0.45 μm polyethersulphone membranes (Millipore, Livingston, UK), samples were analysed for dissolved organic carbon (DOC) in a TOC-V analyser (Shimadzu, Milton Keynes, UK). Zeta potential was analysed with a Malvern Zetasizer Nano ZS (Malvern, UK).

4.2.5 Data analysis

Statistical analysis of the obtained data was done with the software package Minitab 17. One-way ANOVA tests were performed to assess the differences in metal concentrations achieved at varying coagulant dosage and slow mixing conditions (i.e. time and velocity). Pearson's correlation coefficient tests were used to identify relationships between coagulant dose and the concentration of metals in treated effluent. The relationship between DOC and metal concentrations in treated effluent was also assessed. Correlation strength was determined to be weak (0.2 - 0.39), moderate (0.4 - 0.59) or strong (> 0.59) using guidance from Evans (1996). All tests were conducted with a level of significance $p < 0.05$.

4.3 Results and discussion

4.3.1 Wastewater characteristics

Values for wastewater parameters analysed along with total metal concentrations measured in humus effluent samples are shown in Table 4.1. The abundance of target metals in terms of total concentration was $\text{Zn} > \text{Cu} > \text{Ni} > \text{Pb}$ (see Table 4.1). Similar relative abundances and metal concentrations have been reported by other investigators at treatment facilities elsewhere in the UK (Gardner et al. 2013).

4.3.2 Selection criteria for trace metal removal

Both chitosan and PEI had a moderate effect on metal concentrations ($\leq 35\%$ reduction) at all dosage levels and, as a result, were eliminated from the subsequent testing regime. Chitosan molecules include carboxyl and amino functional groups. In our experiments, the pH of the humus effluent was 7.3 ± 0.2 (Table 4.1). At such value, carboxyl groups are deprotonated becoming COO^- , whilst amino groups remain fully protonated as NH_3^+ (Macnow, 2016). Thus, the chitosan molecules had both positive and negative charge

but overall were electrically neutral, owing to the two charges neutralising one another (Macnow, 2016). It was, therefore, anticipated that the electrostatic force between chitosan molecules and humus effluent particles was weak, hindering flocs' formation and explaining why removal of metals by CF with chitosan was constrained in this study.

Table 4.1 Humus effluent characteristics [Mean \pm standard deviation (SD)].

Parameter	Value
pH	7.3 (0.2)
Zeta potential (mV)	-12.9 (0.4)
Turbidity (NTU)	16.6 (7.1)
COD (mg/L)	71.8 (15.7)
DOC (mg/L)	17.9 (2.6)
Total P (mg/L)	5.6 (0.7)
Cu ($\mu\text{g/L}$)	20.5 (3.9)
Pb ($\mu\text{g/L}$)	0.8 (0.1)
Ni ($\mu\text{g/L}$)	3.7 (0.8)
Zn ($\mu\text{g/L}$)	43.1 (8.9)

It is recognised that the ability of polymers to remove metals is influenced by the presence of competing solutes and chelators such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA). These competing substances are typically present in municipal wastewater (Shon et al. 2006) and limit the removal of metals by binding to available sites on the polymers. Since other studies (Almutairi and Lovitt, 2012) have found that PEI has a poor ability to bind Cu, Ni and Zn in the presence of EDTA or NTA, it is thought that the removal of metals by CF with PEI in this study was limited by the presence of competing substances in the effluent. It is recognised that these substances may also have limited the extent to which chitosan removed metals.

4.3.3 Optimisation of coagulant dose for target metal removal

Rates of removal for target metals as a function of FeCl_3 dose are given in Figure 4.1. An increasing dose of FeCl_3 enhanced the overall removal of metals (in particular of Cu and Pb) as higher concentrations of the salt results in ampler floc formation. When comparing FeCl_3 dosages, optimum removals for Cu (66%) and Pb (69%) were

achieved at 0.20 mg/L as significantly lower residual concentrations of both metals were observed in treated effluent ($p < 0.05$). For Zn, the best removal (41%) was obtained after adding 0.10 mg/L FeCl_3 ($p < 0.05$). When it comes to Ni, a cumulative effect in its concentration was found as higher doses of FeCl_3 were added to the humus effluent (see Figure 4.2). This relation proved to be linear as indicated by a strong positive correlation ($r = 0.959$, $p < 0.001$). Studies elsewhere (Buzier et al. 2006; Chys et al. 2013) have reported that FeCl_3 contains considerable Ni amounts and thus significantly contributes to the presence of the metal in treated effluent. This finding was, therefore, expected and indicates that, when used for the treatment of wastewater, FeCl_3 is a potential risk to compliance with environmental quality standards for Ni. Even though 0.20 mg/L provided the highest removal of Cu and Pb, a lower rate of addition was considered optimal for the purposes of this study in order to minimise the inadvertent addition of Ni. The optimum rate of addition was 0.10 mg/L, which produced removal rates of 48% for Cu, 56% for Pb and 41% for Zn.

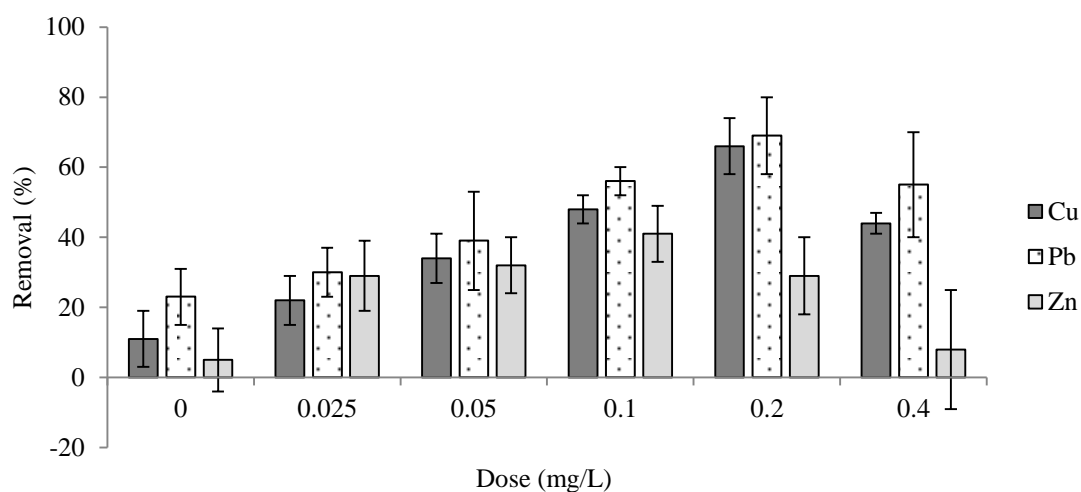


Figure 4.1 Rates of removal for target metals as a function of FeCl_3 dose (Mean \pm SD).

Rates of removal for the target metals as a function of Flocculant dose are shown in Figure 4.3. The highest removal of Cu (85%) was observed at 0.50 mg/L, although no statistically significant difference ($p = 0.209$) was observed when humus effluent was treated with 0.25 mg/L Flocculant. The latter concentration was also the optimum dosage for the removal of Pb (68%). Removal rates (41-44%) for Zn were similar ($p > 0.05$) for doses ranging between 0.25 and 1 mg/L. Given that reduction in Ni concentration was

negligible for Flocculant at all doses ($p > 0.05$; Figure 4.3), 0.25 mg/L was recommended as the optimum dose for the removal of target metals.

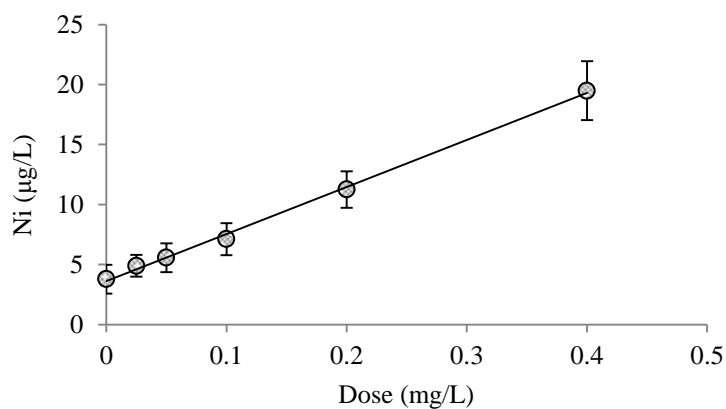


Figure 4.2 Concentration of Ni in treated humus effluent as a function of FeCl_3 dose (Mean \pm SD).

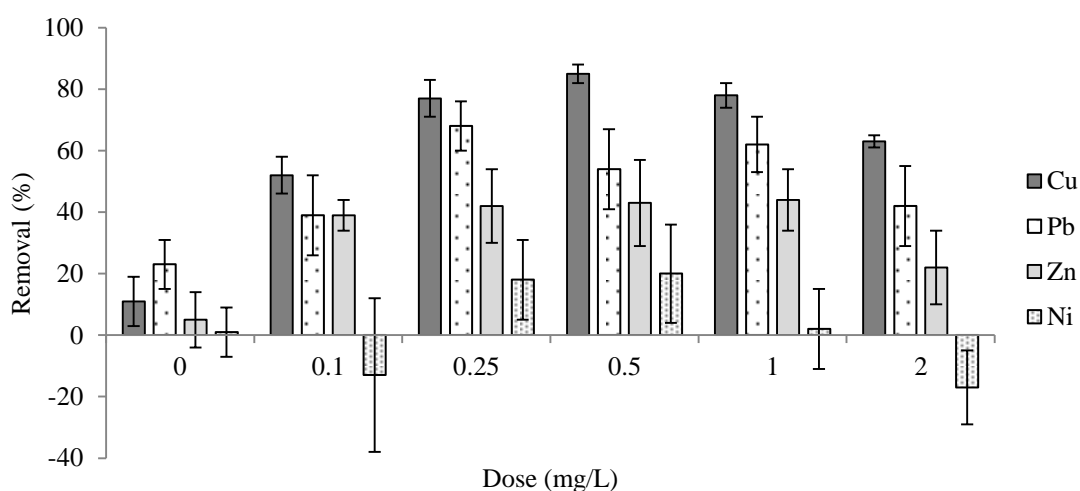


Figure 4.3 Rates of removal for target metals as a function of Flocculant dose (Mean \pm SD).

4.3.4 Performance efficiency

4.3.4.1 Metals

The concentrations of target metals in untreated humus effluent, the investigative control (i.e. CF with no coagulant added) and effluent treated with either FeCl_3 or Flocculant at the optimised dosages are presented in Figure 4.4.

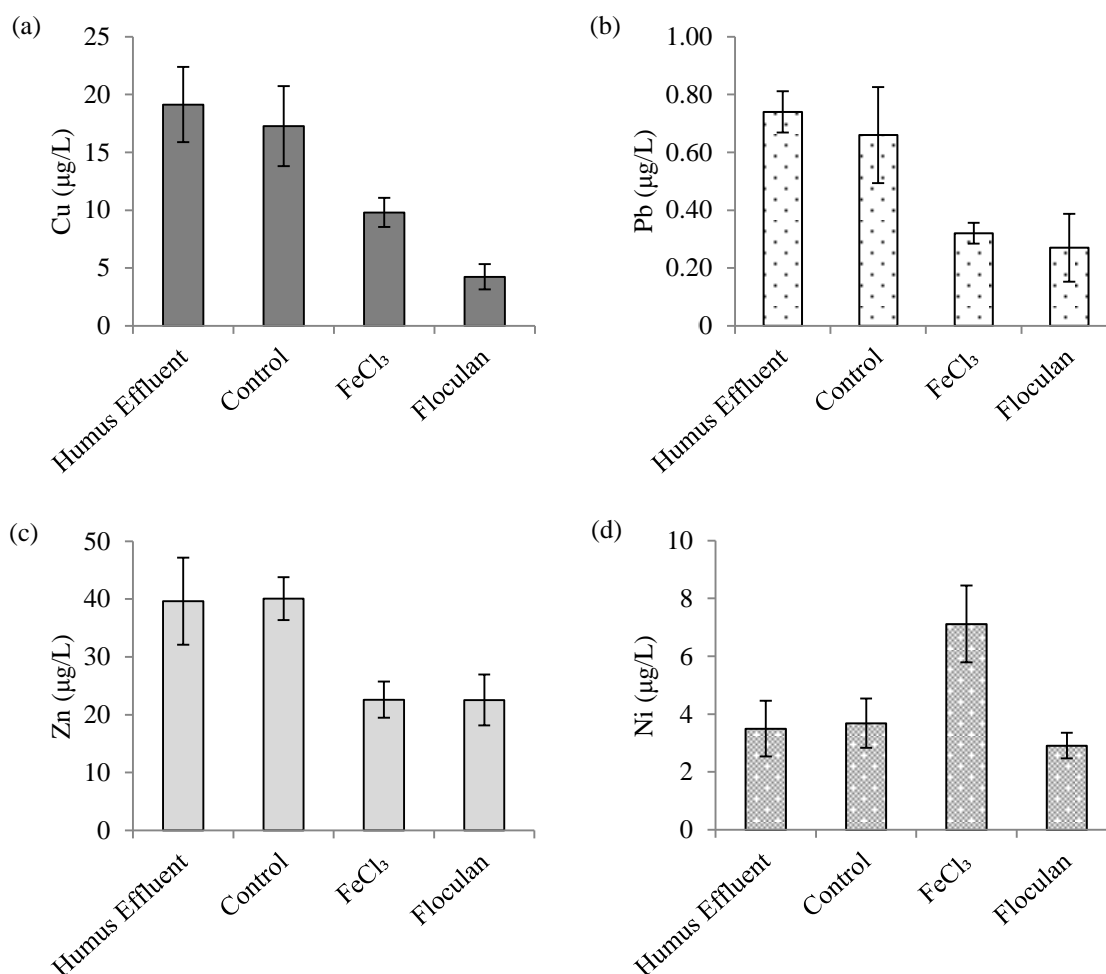


Figure 4.4 Cu (a), Pb (b), Zn (c) and Ni (d) concentrations in humus effluent treated with FeCl₃ (0.10 mg/L) and Floculan (0.25 mg/L) at the recommended doses outlined in this study (Mean \pm SD).

Sizeable amounts of Cu (FeCl₃: 48%, Floculan: 77%) and Pb (FeCl₃: 68%, Floculan: 56%) were removed from humus effluent with both FeCl₃ and Floculan (see Figure 4.4a and b, respectively). Studies (Hargreaves et al. 2017) have reported that these metals are mainly bound to particulate and colloidal materials that readily adsorb to the surface of flocs. Hence, elimination of Cu and Pb by CF was expected. In fact, high rates of removal have been reported elsewhere for FeCl₃ (Cu: 81%, Pb: 88%; El Samrani et al. 2008) and plant based biopolymers (Cu: 90%; Beltrán Heredia and Sánchez Martín, 2009). Our removal percentages were substantially lower than those reported in other studies (El Samrani et al. 2008; Beltrán Heredia and Sánchez Martín, 2009). This is most likely the result of significantly lower metal concentrations (< 25 µg/L Cu and < 1 µg/L Pb; Table 4.1) in the trickling effluent we used in our CF experiments compared with other studies (El Samrani et al. 2008: > 50 µg/L Cu and > 25 µg/L Pb; Beltrán

Heredia and Sánchez Martín, 2009: ~20 mg/L), which makes a high removal percentage more difficult to obtain.

In our case, residual concentrations of Cu after Flocculant addition were significantly lower ($p < 0.001$) than those found for FeCl_3 (Figure 4.4a). This may arise since Flocculant removes organics with functional groups that Cu readily forms complexes with. This was supported by the strong correlation ($r = 0.935$, $p < 0.001$) observed between Cu and DOC concentrations in the treated effluent, and implies that in CF with Flocculant removal in conjunction with DOC was a pathway for the elimination of Cu. Nevertheless, Flocculant is composed of polymeric chains along which functional groups such as amino and phenol groups are found. It is known that free Cu ions have a high affinity for these groups (Lu and Allen, 2002; Hamza et al. 2017), therefore complexation of Cu ions with these functional groups may also be a further point of removal.

As shown in Figure 4.4c, residual concentrations of Zn were comparable for both FeCl_3 and Flocculant ($p = 0.976$). In both cases, a reduction in Zn was anticipated as findings were in agreement with those reported by others. El Samrani et al. (2008) recorded removal rates of up to 93% when using FeCl_3 as a coagulant in the treatment of combined sewer overflow. Beltrán-Heredia and Sánchez-Martín (2009) found that Tanfloc, the active ingredient in Flocculant, had the capacity to reduce Zn concentrations by 75% when treating polluted surface water. It was also noted by these authors that Cu (90%) was removed to a much greater degree than Zn (75%), with a similar trend observed in the present study for Flocculant (Figure 4.4a and c).

As Figure 4.4d shows, Flocculant did not effectively remove Ni from humus effluent ($p = 0.429$). Given that Ni has a low affinity for particulate matter and in effluent at the neutral pH range observed herein (Table 4.1) a large proportion of soluble Ni typically exists in the mobile aqua ion form, such behaviour was expected. These properties reduce the ability of Ni to be adsorbed through the complexation process, thus a $\text{pH} > 11$ is required for effective removal of Ni from the aqueous phase (Patterson, 1985).

4.3.4.2 Turbidity removal

There are two main mechanisms for the removal of particles by FeCl_3 in the CF process namely, charge neutralisation and sweep flocculation. Given the sizeable amount of turbidity removed in conjunction with negative zeta potentials (see Figure 4.5a), it is apparent that charge neutralisation did not play a significant role in the removal of particles from the humus effluent. For example, a dose of 0.10 mg/L FeCl_3 yielded a 75% turbidity removal with a corresponding zeta potential of -12 mV. Increasing the dosage of FeCl_3 improved turbidity removal, although, when dosage beyond operational optimum was added, no further improvement was observed. In fact, when 0.40 mg/L FeCl_3 was added, a turbidity removal of 20% and a zeta potential of 4.39 mV were measured. This result is clearly explained by particle stabilisation. Sweep flocculation involves the enmeshment of particles in precipitates. This mechanism is not influenced

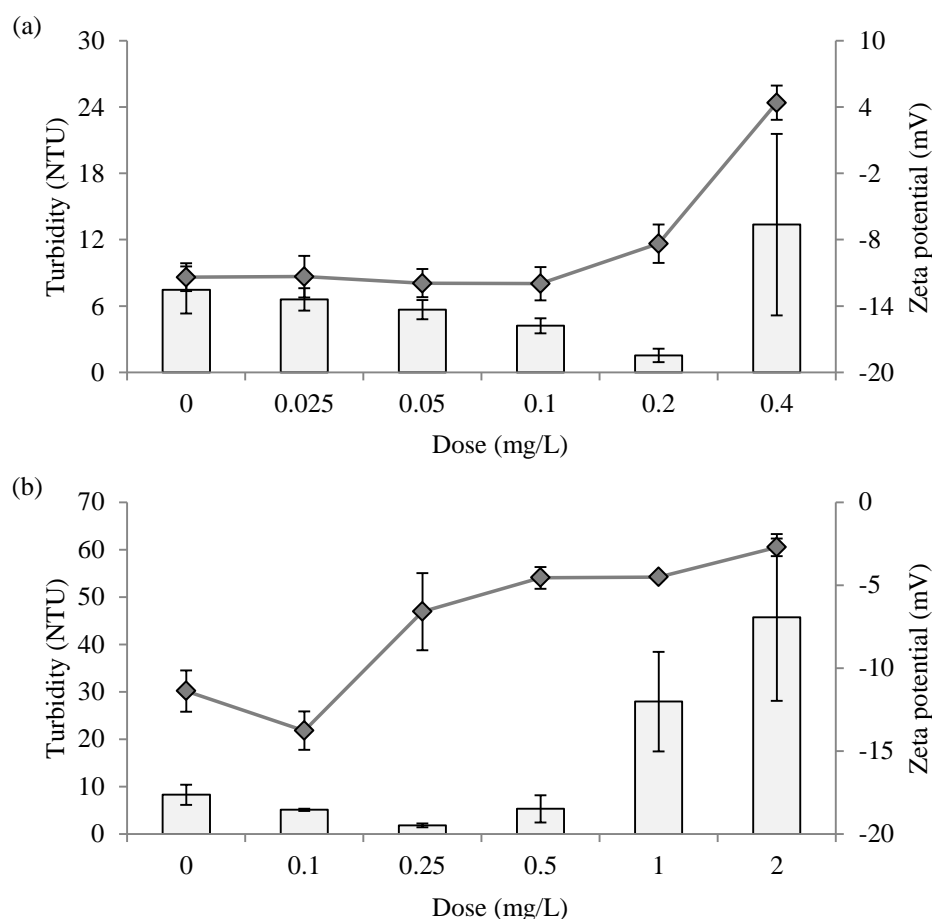


Figure 4.5 Changes in turbidity (bars, light grey) and zeta potential (diamonds, dark grey) at different applied doses of FeCl_3 (a) and Flocculan (b) (Mean \pm SD).

by the properties of particles as negatively charged particles can become entrapped in precipitates (Crittenden et al. 2012). Hence, in our tests, sweep flocculation was assumed to be the main removal mechanism in CF treatment with FeCl_3 .

In CF with Flocculan, zeta potential values increased as coagulant dose increased (see Figure 4.5b). In this case, charge neutralisation played a role in particle removal from humus effluent. Flocculan is composed of polymeric chains that adsorb onto the surface of particles because of interactions such as coulombic, dipole, Van der Waals or hydrogen bonding. These interactions may occur at different points along the chain. Additionally, these chains extend and attach onto other particles which results in bridging between particles. Known as inter-particle bridging, this mechanism is widely recognised as the main process for particle removal by biopolymers (Shak and Wu, 2014). Increasing the Flocculan dose from 0.10 to 0.25 mg/L did enhance the amount of turbidity removed from humus effluent (Figure 4.5b). Higher Flocculan doses provide more polymer chains to be contacted with particles to form particle-polymer-particle aggregates, thus leading to an increase in the quantity of flocs formed. However, an addition of dosage above the optimum would restabilise the particles due to surface saturation by the excess amount of absorbed polymer (Bratby, 2006). This phenomenon will result in a decrease in the amount of turbidity removed, as observed herein for Flocculan dosage ≥ 0.50 mg/l (Figure 4.5b).

4.3.4.3 Organic matter removal

When compared, amounts of removed DOC relative to COD were substantially lower for both FeCl_3 and Flocculan at the recommended dosage (Figure 4.6). Such trend can be attributed to the limited DOC adsorption to flocs, owing to the hydrophilic characteristics of the floc surface and the electrostatic repulsion of DOC when in anionic form (Wang et al. 2015).

The presence of DOC in effluent reduces the bioavailability of residual metal and, as such, DOC is one of the parameters input into the BLM to calculate bioavailable metal concentrations. Compared with FeCl_3 , equivalent or greater removal extents for metals (Figure 4.4) in conjunction with significantly ($p = 0.026$) greater concentrations of DOC in treated effluent (Figure 4.6) indicates that Flocculan is likely to be more effective at

reducing the bioavailability of residual metal in treated effluent. This is important given the current transition toward water quality standards and discharge permits which relate to the metals permissible bioavailable concentration.

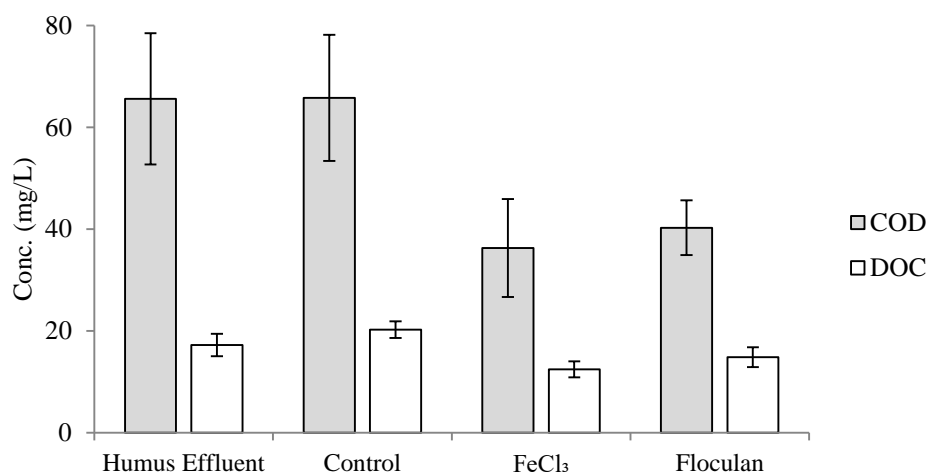


Figure 4.6 COD and DOC concentrations in humus effluent treated with FeCl₃ (0.10 mg/L) and Flocculant (0.25 mg/L) at the recommended doses outlined in this study (Mean \pm SD).

4.3.4.4 Phosphorous removal

The sizeable amount of TP removed by FeCl₃ (see Figure 4.7) was expected, given that this coagulant readily precipitates phosphorous ions enabling effective removal (de-Bashan and Bashan, 2004). Findings from the present study, therefore, indicate that FeCl₃ is a viable treatment option for the simultaneous removal of trace metals (Cu, Pb and Zn) and TP. Nevertheless, removal of P with Flocculant was negligible at all investigated doses (Figure 4.7).

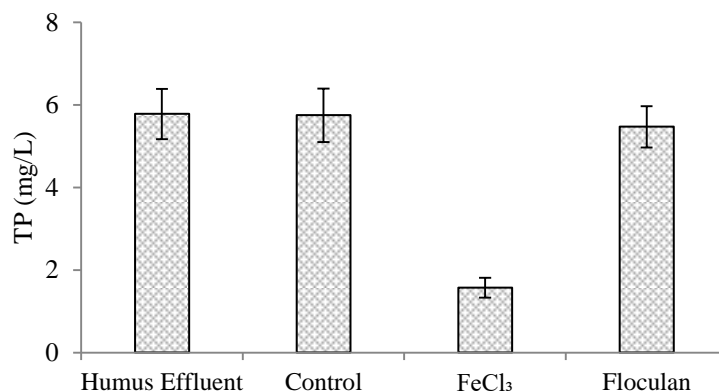


Figure 4.7 TP concentrations in humus effluent treated with FeCl₃ (0.10 mg/L) and Floculan (0.25 mg/L) at the recommended doses outlined in this study (Mean ± SD).

4.3.4.5 pH of treated wastewater

The pH of treated wastewater was considered in this study as it may influence the economic feasibility of coagulants examined. At the recommended optimum dosage of FeCl₃, the pH of treated humus effluent was significantly ($p < 0.001$) reduced with a mean value of 6.6. The acidity of the ferric ions in this reagent explains the change in pH. With Floculan, however, the pH of treated humus effluent remained fairly constant ($p = 0.080$) as values between 7.3 and 7.6 were observed. These findings indicate that pH correction of effluent prior to discharge would not be required when using FeCl₃ or Floculan at the dosage recommended herein, as the discharge allowance for pH is typically between 6 and 9 (UKTAG, 2008).

4.3.5 Effect of slow mixing conditions

Variation in the time (0-50 min) and velocity (0-50 rpm) of the slow mixing stage had no significant effect (one-way ANOVA, $p < 0.05$) on the removal of metals from humus effluent when treated with FeCl₃. Nor did agitation conditions (i.e. time and velocity) significantly influence the amount of Pb and Zn removed by CF with Floculan. These findings suggest that flocs produced by both coagulants have similar resistance to breakage and indicate that slow mixing stage was ineffective at enhancing metals removal. Nevertheless, in CF with Floculan, the operation of the slow mixing stage with agitation times ≥ 30 mins and agitation speeds ≥ 30 rpm reduced Cu concentrations,

such that, they were significantly lower than those observed in the control (i.e. no slow mixing).

4.3.6 Advantages and disadvantages of using coagulation-flocculation with FeCl₃ or Flocculan for trace metal removal

Despite the constant development of new and improved treatment processes, CF still remains an important process for treating wastewater, owing to its simplicity in design and operation, low energy consumption and versatility (Teh et al. 2016). This technology can be applied as a primary, secondary or tertiary treatment and can be operated intermittently. Discontinuous operation enables CF to be used as a responsive treatment, which allows application when sudden spikes in metal load are detected. This is a distinct advantage of CF as a treatment option, as influent metal concentrations are known to fluctuate widely (Salihoglu, 2013) due to the diverse sources of metals in the areas that WWTWs serve.

Previous studies have demonstrated that metal salts and biopolymers are effective for the removal of metal from industrial wastewater (Amuda et al. 2006; Shaheen et al. 2013). Findings from the present study demonstrate that elimination of trace metals in the µg/L range from municipal wastewater can be achieved with CF. At recommended dosage, both FeCl₃ (0.10 mg/L) and Flocculan (0.25 mg/L) were equally effective for the removal of Pb and Zn (Figure 4.4b and c, respectively) from humus effluent. Flocculan, however, outperformed FeCl₃ in the removal of Cu (Figure 4.4a). Whilst elimination of Ni was negligible for Flocculan (Figure 4.3), Ni concentrations were significantly increased in effluent treated with FeCl₃ (Figure 4.2). Such findings indicate that Flocculan is a better option for the removal of trace metals from municipal wastewater.

At present, improving the sustainability and viability of the wastewater treatment process is a particular focus, thus research interests have been shifted toward the use of biopolymers as coagulants (Renault et al. 2009). Flocculan is a commercial product and is, therefore, more practical as a treatment option than non-plant sources such as chitosan, owing to a relatively high-volume market and thus bulk processing. Nevertheless, the cost of Flocculan (£0.65/kg; A. Lee 2017, personal communication) remains substantially higher than that of FeCl₃ (£0.16/kg; A. Major 2017, personal

communication). The low cost of FeCl_3 is typically noted as the main advantage of this salt and it has, thus, been commonly used as a coagulant (Zeng and Park, 2009). A further advantage of FeCl_3 was the simultaneous removal of metal and P from humus effluent (Figure 4.7), something Flocculan was not able to achieve (Figure 4.7).

Further costs must be accounted for when using coagulants in wastewater treatment, in particular, the production of sludge that must be disposed. In CF with biopolymers, flocs formed by inter-particle bridging are dense and closely packed generating low sludge volume and facilitating drying compared to sludge produced with salts (Renault et al. 2009; Lee et al. 2014). In addition, as biopolymers are biodegradable the sludge generated can be efficiently degraded by microorganisms (Renault et al. 2009). Given that Flocculan removed particles through the mechanism of inter-particle bridging (section 4.3.4.2) and is biodegradable, it is expected that, compared with FeCl_3 , sludge handling and disposal costs would be much lower in the application of Flocculan. This advantage may lead to a lower overall treatment cost.

The efficiency of CF with either FeCl_3 or Flocculan was greatly influenced by operating parameters including coagulant dosage (Figures 4.1 and 4.2, respectively). It is, therefore, important to optimise process parameters before large-scale implementations (Teh et al. 2016). Nevertheless, commercialisation for use as a wastewater treatment agent will always be based primarily on whether at full-scale similar treatment performance at comparable (or reduced) cost with established chemical coagulants can be sustained.

4.4. Conclusions

This study was one of the first of its kind to study the effectiveness of the CF treatment process for the elimination of trace metals in the $\mu\text{g/L}$ range from municipal wastewater. Investigation has demonstrated that both FeCl_3 and Flocculan were most effective for the removal of trace metals from humus effluent. Using recommended conditions for dosage (FeCl_3 : 0.10 mg/l, Flocculan: 0.25 mg/L), both coagulants were equally effective in removing Pb and Zn. Flocculan, however, yielded much better removal rates for Cu. Ni removal was negligible with Flocculan, whilst in effluent treated with FeCl_3 , Ni concentrations were significantly increased. These findings depict

Floculan as a better wastewater treatment agent for metal management. Further tests are necessary to assess the performance and cost of Floculan when applied in full-scale wastewater treatment.

High turbidity removals and consistent negative zeta potentials indicated that charge neutralisation did not play a significant role in the removal of particles from humus effluent when treated with FeCl_3 . As such, the sweep flocculation mechanism, which is not influenced by the properties of particles (i.e. negatively charged particles can become entrapped in precipitates), was determined to be the dominant removal mechanism. Floculan, on the other hand, is composed of polymeric chains with cationic charge that neutralise particles and enables aggregation and removal through the mechanism of inter-particle bridging.

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Chapter 5

Impacts of Coagulation-flocculation Treatment on the Size Distribution and Bioavailability of Trace Metals (Cu, Pb, Ni, Zn) in Municipal Wastewater

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5. Impacts of Coagulation-flocculation Treatment on the Size Distribution and Bioavailability of Trace Metals (Cu, Pb, Ni, Zn) in Municipal Wastewater

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Abstract

This study investigated the impact of coagulation-flocculation treatment on metal form and bioavailability in municipal wastewater. Real humus effluent samples were separated into particulate, colloidal and truly dissolved fractions before and after treatment with either ferric chloride (FeCl₃) or the biopolymer Flocculan. Results revealed that both reagents effectively ($\geq 48\%$) eliminated copper (Cu), lead (Pb) and zinc (Zn) from the particulate fraction and removed Cu and Zn from the colloidal fraction in conjunction with colloidal organic carbon (COC). Although organics in the truly dissolved fraction were resistant to removal, Flocculan reduced Cu in this fraction by 72% owing to the complexation of free Cu ions to phenol and amino groups along the polymeric chains, revealing an additional removal pathway. In fact, COC removed in the CF process by Flocculan was replaced with truly dissolved compounds, input as a result of this reagents organic composition. Flocculan, therefore, reduced the soluble concentration of Cu and Zn without changing the DOC concentration, thus reducing the bioavailability of these metals in treated effluent. FeCl₃ did not reduce the bioavailability of target metals, thus did not deliver any environmental benefit. This work provides important information for the selection and development of high performance coagulants to improve metal removal.

5.1 Introduction

Metals including copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) are commonly found in wastewater, with discharges of these metals influencing the chemistry and biology of receiving waters, with potentially toxic implications (Jaishankar et al. 2014). Regulatory drivers therefore typically require concentrations of these metals to be reduced in the wastewater treatment process. Within the European Union, the Water Framework Directive (WFD) (2000/60/EC) has specified bioavailability-based standards for Pb and Ni which are classified as Priority Substances. In the United Kingdom (UK) bioavailability-based standards have also been specified for Cu and Zn (UK Technical Advisory Group [UKTAG], 2008), which are classified as Specific Pollutants under the WFD. The concentration of metal that is bioavailable cannot easily be measured directly and consequently a predictive tool, known as a biotic ligand model (BLM), is used to convert a dissolved phase metal concentration to an equivalent bioavailable metal concentration. BLMs require site-specific information on physico-chemical characteristics as inputs, including the soluble metal concentration, pH, dissolved organic carbon (DOC) and hardness (Di Toro et al. 2001).

In Canada, Australia and New Zealand bioavailability approaches are used in considering ecological impacts (Canadian Council of Ministers of the Environment, 2003; Australian and New Zealand Environment and Conservation Council [ANZECC] and Agriculture and Resource Management Council of Australia and New Zealand [ARMCANZ], 2000) and within the European Union, the Water Framework Directive (WFD) (2000/60/EC) has specified bioavailability-based standards for Pb and Ni which are classified as Priority Substances. Whilst improving environmental relevance, bioavailability-based standards are, nevertheless, expected to significantly reduce acceptable metal concentrations at a range of locations within the UK (Peters et al. 2009). This prospect has raised concern because wastewater treatment works (WWTWs) are traditionally designed to address problems of carbon contamination and nutrient enrichment rather than for trace metal elimination, and studies have shown that metal removal rates vary considerably at WWTWs (Gardner et al. 2013). In order to achieve removal rates to comply with more stringent discharge quality requirements, the development of novel wastewater treatment technologies is urgently required.

To enhance metal removal, a large body of previous work indicates the relevance of understanding metal form throughout wastewater treatment for the selection of suitable technologies (Chipasa, 2003; Karvelas et al. 2003; Santos and Judd, 2010). Analysis of metal form traditionally involves separation with a 0.45 μm filter. A soluble fraction passes through the filter, whilst particulates are retained on the filter (i.e. $> 0.45 \mu\text{m}$). Metals such as Cu and Pb are known to have a high affinity for the particulate fraction and, thus, can be removed as part of the wastewater treatment process by physical separation (Choubert et al. 2011). In contrast, Ni and Zn predominantly exist within the soluble fraction which potentially requires expensive and energy intensive processes such as adsorption or ion exchange for effective removal. Faced with the expectation of more stringent regulation, treatment technologies which can simultaneously remove particulate and soluble metal from wastewater at low treatment cost are desired by WWTWs operators.

Soluble components can be separated into two further size fractions namely, a colloidal fraction, which is composed of material found in the size range 1 kDa to 0.45 μm , and a truly dissolved fraction, which contains constituents with a molecular weight (MW) < 1 kDa (Worms et al. 2010). Metal distribution within the soluble fraction is influenced by the presence of functional groups (ligands) that may complex metal ions. It has been reported that the distribution of metals between colloidal and truly dissolved fractions is greatly influenced by the distribution of DOC within these same fractions (Worms et al. 2010). Organics found in the truly dissolved size fraction include amino acids, carbohydrates, hydrated metal ions and synthetic ligands such as ethylenediaminetetraacetic acid (EDTA) (Imai et al. 2002; Shon et al. 2006). Conversely, organic material in the colloidal fraction is predominantly composed of macromolecules including polysaccharides and proteins (Jarusutthirak et al. 2002; Nam and Amy, 2008). In a recent study (Hargreaves et al. 2017) a large proportion of Cu, Pb, Ni and Zn was observed to reside in the colloidal fraction of effluent and calculated molar ratios of metals to organic carbon indicated that a large proportion of these metals may be adsorbed to colloidal material or complexed with macromolecules present in the colloidal size fraction. Such findings suggest that technologies capable of removing organic materials within the colloidal size fraction could reduce the concentration of target metals (Cu, Pb, Ni and Zn) in effluent discharges.

One such technology is coagulation-flocculation (CF), a widely used technique for the treatment of industrial effluent. Coagulation involves combining insoluble particles and dissolved matter into larger aggregates through the addition of chemical reagents (Renault et al. 2009). Aggregates are bonded together by flocculation, which consists of a stirring/agitation procedure that encourages particles to agglomerate, thus allowing their removal in subsequent sedimentation and filtration phases (Renault et al. 2009). Mechanisms through which particulate and colloidal materials are aggregated and, thus, removed can involve a combination of adsorption, entrapment, charge neutralisation and complexation processes (Alexander et al. 2012), and are dependent on the reagent used.

Chemical reagents frequently applied in the CF process are metal salts such as ferric chloride (FeCl_3) and polyaluminium chloride, which aggregate particles by charge neutralisation and sweep flocculation (Duan and Gregory, 2003). FeCl_3 is commonly used to remove phosphorus from sewage effluents and studies have shown this reagent can enhance the removal of metals from combined sewer overflow (El Samrani et al. 2008), but few studies have investigated application for the treatment of municipal wastewater. On a global scale, however, waste management systems are under change, with producer responsibility and consumer accountability driving the development of sustainable and eco-friendly management systems (Zaman, 2013). An increase in the awareness of the detrimental consequences that metal salts may have to the environment, such as increasing non-target metal concentrations in treated wastewater and significant alterations to the pH of treated water (Renault et al. 2009; Vijayaraghavan et al. 2011), has resulted in ongoing investigations into alternatives.

Tanfloc, a tannin-based product with a trademark belonging to TANAC (Brazil) has attracted attention because of its renewability, biodegradability and its capacity to eliminate metals (Beltrán Heredia and Sánchez Martín, 2009). For example, zeta potential measurements have showed the cationic nature of Tanfloc and, given the polymeric structure of this coagulant, mechanisms of charge neutralisation and inter-particle bridging are suggested to be involved in the CF process (Hameed et al. 2016). Flocculan is a commercially available product which is composed of up to 30% Tanfloc and is, therefore, a practical treatment option. Studies investigating the application of this reagent to municipal wastewater are, however, limited. It is also noted that there is a

scarcity of studies that assess the impact of CF on metal form and bioavailability within the effluent matrix. Specific information on the fate of metals following CF is needed to assess the benefits of this treatment technology and to provide key information on coagulant selection for the treatment of municipal wastewater effluents. Furthermore, understanding the relationship between metal fractionation and CF may help develop high performance reagents for future application to improve metal removal in wastewater treatment.

The aim of this study was, therefore, to investigate the impact of CF on metal forms (particulate, colloidal and truly dissolved fractions) and bioavailability in municipal wastewater. The study set out to compare the effect of the biopolymer Flocculan on metal removal and to compare that with the conventional coagulant, FeCl_3 . To further characterise the properties of coagulants and flocs produced from the treatment, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) were used.

5.2 Materials and Methods

5.2.1 Materials

Nitric acid (HNO_3), sodium hydroxide (NaOH) and hydrochloric acid (HCl) were all obtained from Fisher Scientific (Loughborough, UK) and were of reagent grade. Plastic and glassware was kept in a 2% (v/v) HNO_3 solution between uses, and were rinsed with ultrapure water prior to use. Flocculan was obtained from Lansdowne Chemicals (Oxon, UK). Ferric chloride (FeCl_3) solution (40%) was provided by Darrant Chemicals (Lincoln, UK).

5.2.2 Wastewater samples

Humus effluent samples were taken from a WWTWs in the UK which operated the trickling filter treatment type. Samples were collected on 8 occasions over a five-month study period (from October 2016 – February 2017) with at least one collection each month. Samples were collected in 5 L plastic containers which had previously been rinsed with 0.01 M HCl and ultrapure water (0.05 μS conductivity level). Samples were

transported to, and were kept, in a refrigerated environment (4 °C) at Cranfield University laboratories prior to analysis.

5.2.3 Coagulation-flocculation experiments

To replicate the CF process Phipps and Bird jar test apparatus (Richmond, United States) was used. Plastic beakers (rinsed with 0.01 M HCl and ultrapure water) were filled with one litre of humus effluent, placed on the floc illuminator and once the coagulant dose was added, were agitated at a fixed intensity (100 rpm) and duration (2 min). The coagulant dose was fixed at the optimum level established in a previous study by the authors herein (Chapter 4); 0.25 mg/L for Flocculan and 0.10 mg/L for FeCl₃. Once rapid mixing finished, the fixed intensity and duration of slow mixing (30 rpm for 30 min) was immediately established. After slow mixing the beakers were removed from the floc illuminator and were positioned in a safe place for 30 minutes, allowing for sedimentation. After sedimentation, the supernatant was extracted from about 25 mm below the surface with a syringe. For the first 3 humus effluent samples collected, jar tests were conducted in duplicate. For the additional five samples collected, jar tests were conducted in triplicate. Therefore a total of 42 jars were treated with either FeCl₃ or Flocculan (i.e. 21 jars for each coagulant). For each sample collected a minimum of 1 beaker was processed through the jar test procedure outlined above without the addition of a coagulant, and was therefore treated by stirring only. This was used as the experimental control.

5.2.4 Particle size fractionation

Particle size fractionation of the samples was conducted following a variation of the method described by Barker and Stuckey (1999). To obtain the soluble phase samples were filtered through 0.45 µm polyethersulphone membranes (Millipore, Livingston, UK) by vacuum filtration (American Public Health Association [APHA], 2005). Regenerated cellulose membranes (1 kDa) (Millipore, Livingston, UK) were used to fractionate the samples into colloidal and truly dissolved fractions. Membranes were washed in sequences of ultrapure water (0.05 µS conductivity level), 0.01 M NaOH and 0.01 M HCl. This alkaline/acid cleaning sequence was repeated after each use. Truly dissolved fractionations were undertaken using an Amicon 8400 stirred pressure cell

(Millipore, Livingston, UK). Filtration was driven by nitrogen gas at a pressure of 160 kPa. To limit concentration polarisation of solute at the membrane surface, an integrated bar stirrer was operated and a filtrate/retentate ratio of 0.4 was adopted.

5.2.5 Analytical methods

The pH measurements were conducted with a Jenway 4330 pH and conductivity meter (Stone, UK). Turbidity was measured using a HACH 2100N turbidimeter (Manchester, UK). Total chemical oxygen demand (COD) and total phosphorous (TP) concentrations were determined using cell test kits (Fisher Scientific, Leicestershire, UK). Dissolved organic carbon (DOC) content was determined using a TOC-V analyser (Shimadzu, Milton Keynes, UK). Target metals (Cu, Pb, Ni, Zn) were measured by inductively coupled plasma-mass spectrometer (ICP-MS) using a Nexion 350D system (Perkin Elmer, Beaconsfield, UK). The limit of detection for all the metals was 0.01 µg/L. Certified calibration standards were used to check analytical accuracy. Both calibration solutions and samples were spiked with a four mixed elements solution (containing selenium, germanium, rhodium, bismuth) for internal standardisation across the full mass range. Prior to ICP-MS analysis, samples were digested with a CEM-MARS microwave (CEM, Buckingham, UK) in order to determine the total concentration of the target metals. Sample blanks were processed through the preparation and analytical procedures. Phase distributions were calculated as follows: particulate = total - soluble, colloidal = soluble - truly dissolved. In effluent, bioavailable metal concentrations were estimated by using the metal bioavailability assessment tool (M-BAT). The MBAT is a simplified version of the BLMs for Cu, Ni and Zn and takes into account the influence of DOC, calcium (not analysed in this study so a default value of 99.6 mg/l was used - based on previous findings at the site) and pH (WFD and UKTAG, 2014). The EQS for Pb is an EU standard under the WFD, thus, it considers the influence of DOC on Pb toxicity but does not require the consideration of pH or hardness. A separate tool has, therefore, been developed for Pb (WFD and UKTAG, 2014) and this was used to estimate the bioavailable concentration of Pb in the effluent.

Dried flocs obtained after the coagulation-flocculation process were examined under a FEI XL30 SFEG scanning electron microscope (Cambridge, UK) to reveal the morphology of flocs produced by FeCl₃ and Flocculan. The infrared absorption spectrum

of coagulants, suspended solids in the humus effluent and flocs in the treated effluent were obtained with a JASCO 4100 Fourier transform infrared spectrometer (Dunmow, UK) to characterise the molecular structure. These analyses characterised the differences in flocs formed to evaluate the mechanisms of metal removal with FeCl₃ and Flocculan.

5.2.6 Data analysis

Statistical analysis of the obtained data was completed with the software package Minitab 17. One-way ANOVA tests were performed to assess the differences in metal concentrations between fractions after treatment with either FeCl₃ or Flocculan. Pearson's correlation coefficient tests were used to express the relationship between the concentrations of metals and DOC. Using guidance from Evans (1996) correlation strength was determined to be weak (0.2-0.39), moderate (0.4-0.59) or strong (> 0.59). Both tests were conducted with a level of significance $p < 0.05$.

5.3 Results and discussion

5.3.1 Humus effluent characteristics

The concentrations of target metals as well as sanitary determinands in the humus effluent are shown in Table 5.1. In humus effluent, the abundance of target metals in terms of total concentration was Zn > Cu > Ni > Pb (see Table 5.1). Other investigators (Gardner et al. 2013) have observed similar relative abundances and metal concentrations at WWTWs elsewhere in the UK.

5.3.2 Impact of coagulation-flocculation on dissolved organic carbon

In the CF process, FeCl₃ removed a sizeable amount of DOC (42%) from humus effluent. Conversely, overall removal of DOC with Flocculan was negligible (1%; Table 5.1), as indicated by no significant ($p = 0.589$) change in the overall DOC concentration (Figure 5.1). Nevertheless, in both cases significant ($p < 0.001$) removal of colloidal organic carbon (COC) was observed, with removal rates of 61 and 37% recorded for FeCl₃ and Flocculan respectively. Organic constituents in the colloidal size range are

composed of macromolecules such as polysaccharides and proteins (Jarusutthirak et al. 2002; Nam and Amy, 2008). In CF, co-precipitation of macro-molecular substances in the colloidal size fraction is favoured, due to their large number and variety of functional groups which enhances attachment to precipitates (Haberkamp et al. 2007). In addition, constituents with higher MW can readily overcome electrostatic repulsion to become adsorbed (Wang et al. 2015). Removal of macromolecular particles in the CF process was therefore anticipated and has been observed elsewhere in the treatment of secondary effluent with FeCl_3 (Haberkamp et al. 2007).

Table 5.1 Concentrations of sanitary determinands in humus effluent before and after treatment with FeCl_3 and Flocculan, and the associated rates of removal observed [Mean (standard deviation)].

Parameter	Humus Effluent	FeCl ₃	Floculan	Removal Rate (%)	
				FeCl ₃	Floculan
<i>Sanitary parameters</i>					
pH	7.4 (0.1)	6.7 (0.1)	7.4 (0.2)		
Turbidity (NTU)	8.7 (1.9)	3.6 (1.3)	2.9 (1.6)	59 (15)	69 (14)
COD (mg/L)	58 (7.6)	32.8 (13.6)	43.8 (8.6)	43 (19)	22 (11)
DOC (mg/L)	13.1 (1.6)	8 (1.6)	12.9 (1.6)	42 (9)	1 (11)
Total P (mg/L)	4.7 (0.6)	0.6 (0.3)	4.3 (0.7)	86 (4)	9 (4)
<i>Metals (μg/L)</i>					
Cu (total)	19.1 (3.7)	8.5 (2.4)	3.4 (0.8)	53 (16)	81 (6)
Cu (soluble)	10.3 (2.3)	5 (1.3)	1.4 (0.4)	51 (6)	86 (2)
Pb (total)	0.8 (0.3)	0.3 (0.2)	0.3 (0.2)	58 (17)	65 (13)
Pb (soluble)	0.4 (0.2)	0.2 (0.1)	0.2 (0.1)	54 (18)	56 (16)
Ni (total)	3 (0.6)	6.4 (1.1)	2.7 (0.9)	-112 (34)	9 (28)
Ni (soluble)	1.8 (0.5)	4.8 (0.9)	1.6 (0.4)	-178 (52)	17 (24)
Zn (total)	40.3 (8.2)	26.9 (4.8)	23.1 (3.6)	36 (9)	42 (10)
Zn (soluble)	26.4 (6.8)	18 (3.9)	14.5 (2.9)	31 (13)	45 (11)

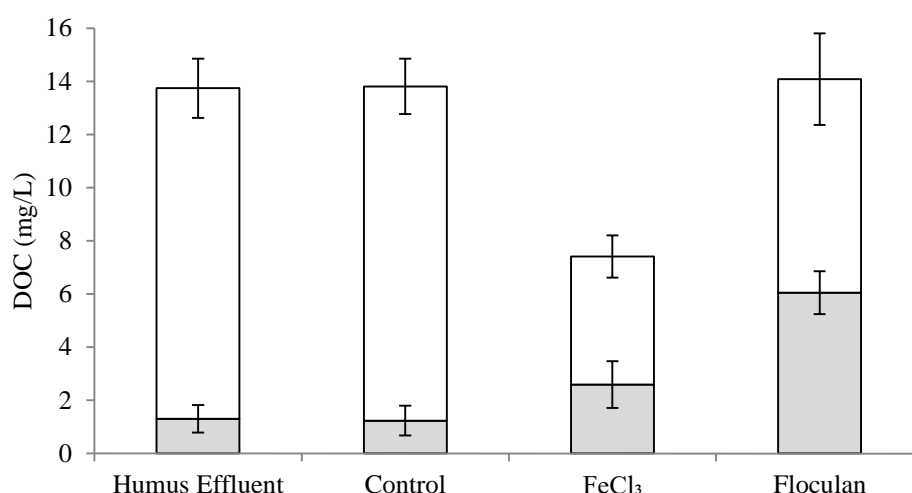


Figure 5.1 Distribution of DOC in colloidal (white) and truly dissolved (grey) size fractions in humus effluent, the experimental control and effluent treated with either FeCl₃ or Flocculan (Mean \pm 95% confidence interval [CI]).

The concentration of DOC in the truly dissolved fraction was not significantly changed following treatment with FeCl₃ (Figure 5.1). Other studies (Imai et al. 2002; Shon et al. 2006) have identified that the truly dissolved fraction is composed of free metal ions and low MW organic constituents. This study, therefore, supports the findings of others (Michael-Kordatou et al. 2015) by revealing that low MW organics are removed to a minor extent in the CF process. Removal of DOC from the truly dissolved fraction was also negligible in CF with Flocculan. In fact, an increase in the concentration of DOC in this fraction was observed following treatment (1.3 to 6.1 mg/L; Figure 5.1).

5.3.3 Distribution of metals in humus effluent

The distribution of target metals within the particulate ($> 0.45\mu\text{m}$), colloidal (1 kDa – $0.45\mu\text{m}$) and truly dissolved (< 1 kDa) fractions in humus effluent, the experimental control and effluent treated with either FeCl₃ or Flocculan, are presented in Figure 5.2.

In humus effluent, a sizable proportion of Cu (47%), Pb (61%), Ni (37%) and Zn (33%) was distributed in the particulate fraction (Figure 5.2). The distribution of metals in this fraction and trend recorded (i.e. Pb $>$ Cu $>$ Ni $>$ Zn) were similar to that observed by Hargreaves et al. (2017). Soluble Cu (46%), Pb (29%), Ni (36%) and Zn (46%) were predominantly distributed in the colloidal size fraction of the humus effluent, whilst for

all target metals distribution in the truly dissolved fraction was relatively low (Figure 5.2). Other studies (Gagnon et al. 2014; Hargreaves et al. 2017) have reported similar distributions in effluent.

5.3.4 Impact of coagulation-flocculation on metal size distribution

5.3.4.1 Copper

With an initial total concentration of $19.1 \pm 3.7 \mu\text{g/L}$ (Table 5.1), good overall rates of removal were observed for Cu in CF with either FeCl_3 (53%) or Flocculan (81%). High removals have been reported elsewhere for FeCl_3 (Cu: 81%; El Samrani et al. 2008) and plant based biopolymers (Cu: 90%; Beltrán Heredia and Sánchez Martín, 2009). The result was therefore in line with expectations.

For the particulate fraction, high removals were observed (FeCl_3 : 60%; Flocculan: 70%), as indicated by significantly lower Cu concentrations in effluent treated with FeCl_3 or Flocculan ($p < 0.001$; Figure 5.2a). In fact, particulate Cu concentrations were similar in the treated effluents (FeCl_3 : $3.6 \pm 2 \mu\text{g/L}$; Flocculan: $2 \pm 0.8 \mu\text{g/L}$). Suspended particles adsorb to the surface of flocs, which are aggregated and removed in the CF process (Renault et al. 2009). In addition, the removal of particulate Cu in conjunction with suspended particles has been reported in a previous study at the site (Hargreaves et al. 2017). Hence, removal of particulate Cu in the CF process was anticipated.

An appreciable amount of Cu was also removed from the colloidal size fraction when treated with FeCl_3 (61%) or Flocculan (88%), as indicated by significantly lower concentrations ($p < 0.001$) compared with initial humus effluent values. In fact, strong correlations were observed between colloidal Cu and COC concentrations (FeCl_3 : $r = 0.704$, $p = 0.001$; Flocculan: $r = 0.715$, $p < 0.001$) in treated effluent, which indicates that removal of Cu occurred in conjunction with the elimination of organics from the colloidal size fraction. Organic constituents in the colloidal size range include proteins, and polysaccharides (Jarusutthirak et al. 2002; Nam and Amy, 2008); such substances are highly reactive regarding metal complexation due to their polyfunctional character and large binding site density (Worms et al. 2010). Results from the present

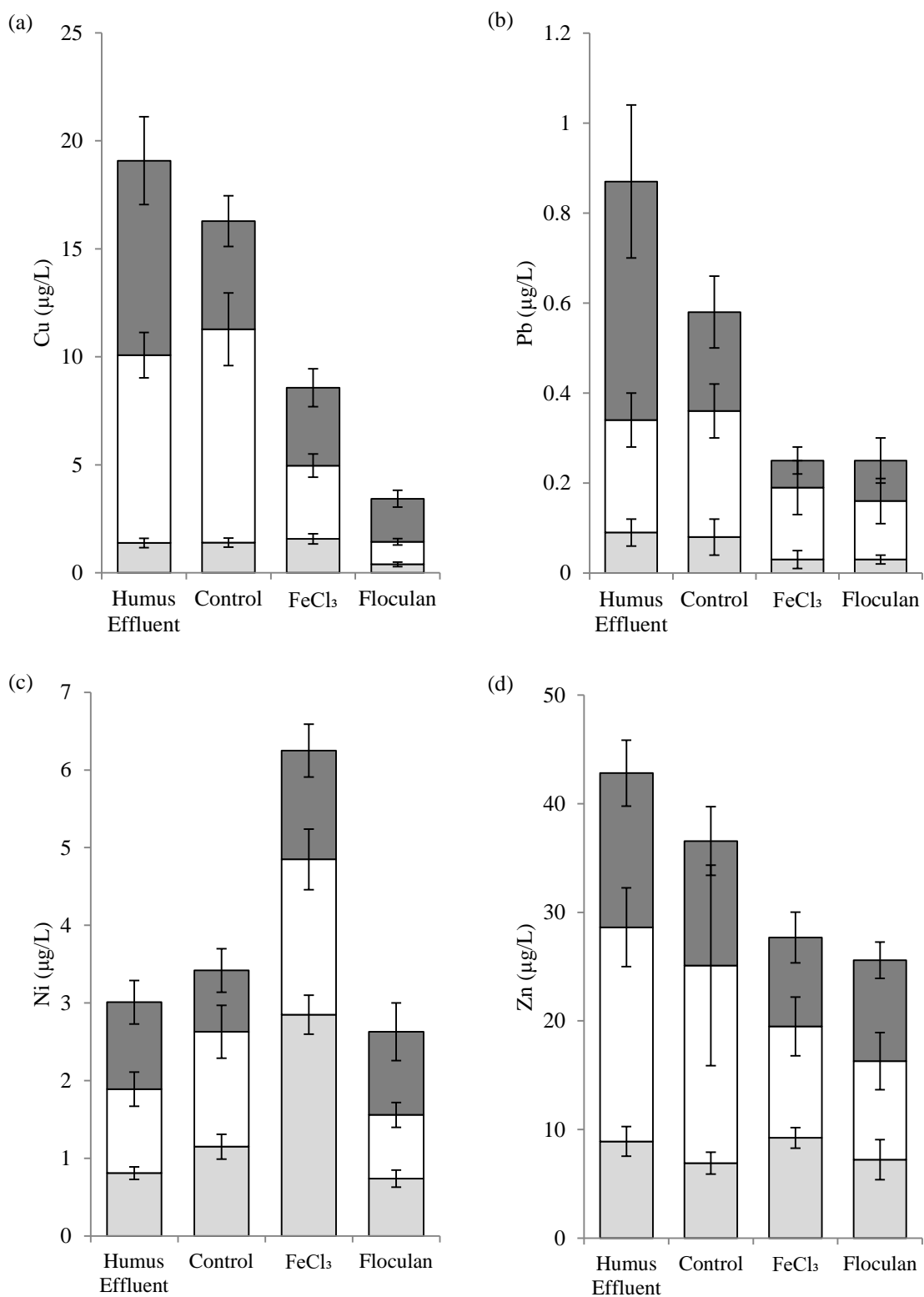


Figure 5.2 Distribution of Cu (a), Pb (b), Ni (c) and Zn (d) between particulate (dark grey), colloidal (white) and truly dissolved (light grey) size fractions in humus effluent, the experimental control and effluent treated with either FeCl_3 or Flocculan (Mean \pm 95% CI).

study therefore indicate that technologies capable of removing organic particles within the colloidal fraction are capable of reducing soluble Cu concentrations in effluent.

Despite FeCl_3 achieving a higher rate of removal for COC (Figure 5.1), a significantly lower Cu concentration was observed in the colloidal fraction of effluent treated with Flocculan ($p < 0.001$, Figure 5.2a). It was anticipated that this may arise since Flocculan has the ability to remove organic materials with functional groups that Cu readily complexes with. In fact, other studies (Hameed et al. 2016) have revealed that Tanfloc (the active ingredient in Flocculan) contains carbonyl and amino functional groups. These are indicative of polysaccharides and proteins that can play a significant role in the complexation of Cu in effluent (Michael-Kordatou et al. 2015). Furthermore, polysaccharides are the dominant material of extracellular polymers produced by microorganisms during biological wastewater treatment (Wang and Wu, 2009), thus were anticipated to be a prominent colloidal organic constituent in the humus effluent.

In CF with FeCl_3 , removal of Cu from the truly dissolved fraction was negligible (see Figure 5.2a). Thus, FeCl_3 did not affect the Cu found within this fraction. Studies (Imai et al. 2002; Shon et al. 2006) have revealed that the truly dissolved fraction is comprised of free metal ions and organic constituents including carbohydrates and amino acids, which metals may adsorb to or complex with. Given that organic materials distributed in the truly dissolved fraction were revealed to be resistant to removal (Figure 5.1), negligible removal of metals associated to them can be expected. Nevertheless, Flocculan reduced the concentration of Cu in the truly dissolved fraction by 72% (from 1.4 to 0.4 $\mu\text{g/L}$; Figure 5.2a). It was, therefore, assumed that a further removal mechanism was involved in CF with Flocculan. Flocculan is a biopolymer composed of polymeric chains along which functional groups including phenolic and amino groups are found. Free Cu ions have a high affinity for these functional groups (Lu and Allen, 2002; Hamza et al. 2017) so it was anticipated that, in CF with Flocculan, complexation of free Cu ions with these functional groups occurred resulting in a lower Cu concentration in the truly dissolved fraction after treatment (Figure 5.2a).

5.3.4.2 Lead and zinc

Sizeable amounts of Pb and Zn were removed from humus effluent in the CF process (see Table 5.1). Such findings were expected as other researchers have reported that FeCl₃ (Johnson et al. 2008) and biopolymers (Kazemipour et al. 2008) were effective for the removal of Pb and Zn from synthetic wastewater. The residual concentrations of Pb and Zn were comparable for FeCl₃ and Flocculant (Figure 5.2b and d, respectively).

Significant ($p < 0.001$) removal of Pb occurred from the particulate fraction in CF with either FeCl₃ (89%) or Flocculant (83%) (Figure 5.2b). Pb was predominantly distributed in the particulate fraction of humus effluent (Figure 5.2b) and, when in this form, it is known to be removed in conjunction with suspended particles (Hargreaves et al. 2017). Hence, such finding was in line with expectations. In the case of Zn, the respective removals from the particulate fraction for FeCl₃ and Flocculant were 42 and 35% (Figure 5.2d), as indicated by significantly lower concentrations following treatment ($p < 0.05$). Nonetheless, Zn removals were lower than those observed for Cu (FeCl₃: 60%, Flocculant: 70%) and Pb (FeCl₃: 89%, Flocculant: 83%), as a relatively low proportion of Zn was distributed in the particulate fraction of humus effluent. Such trend in metal removal from the particulate fraction supports the findings of other studies at WWTWs elsewhere (Karvelas et al. 2003).

As Figure 5.2d shows, a large proportion of Zn in the colloidal size fraction was eliminated after CF with FeCl₃ (48%) and Flocculant (54%). Moderate correlations (FeCl₃: $r = 0.461$, $p = 0.035$; Flocculant: $r = 0.509$, $p = 0.006$) were observed between colloidal Zn and COC concentrations indicating that, as for Cu, Zn was eliminated in conjunction with COC. Other studies (Louis et al. 2014; Constantino et al. 2015) have indicated specific ultraviolet absorbance (SUVA) to be a poor predictor of Zn complexation capacity, which suggests that macromolecules distributed in the colloidal size fraction may be significant for the binding of Zn ions in effluent. Nevertheless, removal rates in the colloidal fraction were much lower for Zn (FeCl₃: 48%, Flocculant: 54%) compared with Cu (FeCl₃: 61%, Flocculant: 88%). This was anticipated to result from the adverse impact of alternate competing soluble metals. At municipal WWTWs effluent contains a large number of metallic species beyond those tested in this study, for example Ca and Mg. Hence, a highly competitive process occurs between metal ions and binding sites in effluent: metal ions compete with each other for complex formation

and thus stability constants provide information on adsorption equilibria (Turhanen et al. 2015). The conditional stability constants for Zn with dissolved organic matter were revealed to be lower than that of Cu in effluent at municipal WWTWs (Chaminda et al. 2013). Zn may, therefore, be more readily displaced at the surface of binding sites by competing soluble metals, and such behaviour has been supported by the findings of others. For example, Zhao et al. (1999) revealed that Ca and Mg may have a negative effect on the removal of Zn via competitive sorption to binding sites on the surface of biomass. In contrast, it has been reported that even in the presence of high Ca and Mg concentrations, Cu may be capable of binding to complexing agents (Turhanen et al. 2015). Thus, Cu can readily outcompete other metals for binding sites on the surface of colloidal organic compounds, which were removed in the CF process.

The difference between the concentration of colloidal Pb in humus effluent (0.3 ± 0.1 $\mu\text{g/L}$) and that observed in humus effluent treated with FeCl_3 (0.2 ± 0.1 $\mu\text{g/L}$) or Flocculant (0.1 ± 0.1 $\mu\text{g/L}$) was negligible. Furthermore, no significant change ($p > 0.05$) in the concentration of Zn and Pb in the truly dissolved fraction was observed (Figure 5.2b and d). These findings indicate that FeCl_3 and Flocculant had little or no effect on the truly dissolved Pb and Zn.

5.3.4.3 Nickel

Despite a sizeable proportion of Ni measured in the particulate and colloidal size fractions of humus effluent, no significant reduction in its concentration or change in its distribution were observed following treatment with Flocculant (Figure 5.2c). This indicates that any existing Ni complexes were unaffected by Flocculant.

A substantial increase in the concentration of Ni was observed in CF with FeCl_3 , which was attributed to impurities in this reagent. Other studies (Buzier et al. 2006; Chys et al. 2013) have reported that FeCl_3 contains substantial amounts of Ni and contributes toward the presence of this metal in treated effluent. In this study Ni concentrations in the truly dissolved fraction were significantly increased by 72% ($p < 0.001$) after addition of FeCl_3 . This is of concern as this fraction is considered the most bioavailable to aquatic life (Gagnon et al. 2014), therefore when used in wastewater treatment FeCl_3 may pose a risk to receiving watercourse ecology.

5.3.5 Impact of coagulation-flocculation on metal bioavailability

The bioavailable concentrations of target metals in humus effluent, the experimental control and effluent treated with either FeCl₃ or Flocculan are presented in Figure 5.3. In order to calculate bioavailable metal concentrations, BLMs account for the interaction of trace metals with DOC which contains a variety of ligands that bind metal ions, thereby reducing their ability to interact with organisms. Thus, increasing the DOC concentration significantly reduces the bioavailability of the metal. At low metal:DOC ratios, there is an excess of complexation capacity so that free metal ion activity is reduced (Doig and Liber, 2007). For example, Pernet-Coudrier et al. (2008) reported that Cu toxicity towards *Daphnia magna* was reduced in the presence of dissolved organic matter derived from wastewater treated effluent. More recently, a study by Constantino et al. (2017) demonstrated that effluent-derived DOC offers a relatively greater complexation capacity per milligram of DOC in comparison with DOC obtained from natural sources. As seen in Figure 5.1, COC removed in the CF process by Flocculan was replaced with truly dissolved compounds as a result of the organic nature of this reagent. Flocculan was, therefore, able to reduce the soluble concentration of Cu (86%), Pb (56%) and Zn (45%) without significantly ($p = 0.589$) reducing the concentration of DOC in treated effluent (Figure 5.1). Thus, a significant reduction in the concentration of bioavailable Cu ($p < 0.001$), Pb ($p = 0.001$) and Zn ($p < 0.001$) was observed (Figure 5.3a, b and d, respectively). These findings indicate that Flocculan was capable of simultaneously reducing the concentration and bioavailability of these metals in treated effluent. The environmental benefit of utilising Flocculan should therefore be considered in decision making on municipal wastewater treatment. The bioavailable Ni concentration was unchanged ($p = 0.101$) following treatment with Flocculan (Figure 5.3c).

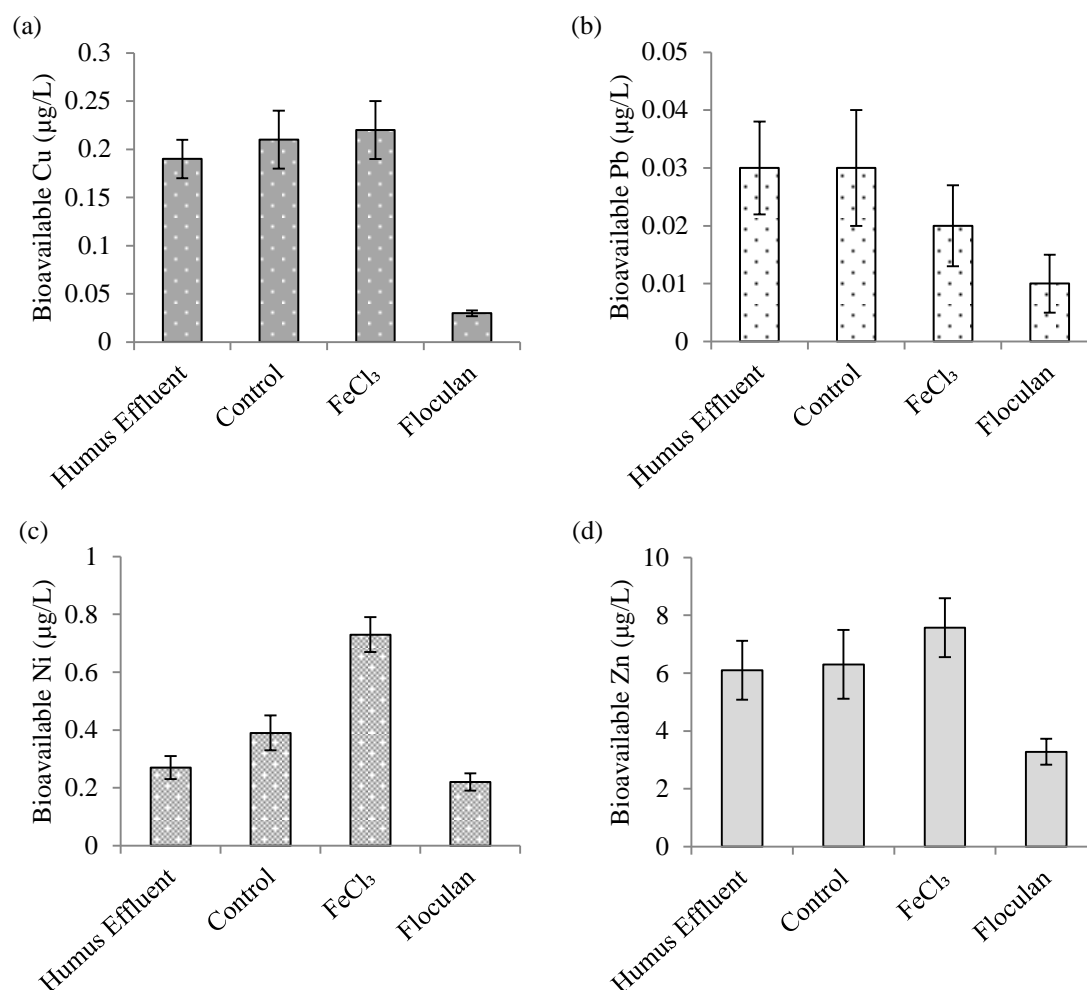


Figure 5.3 Bioavailable Cu (a), Pb (b), Ni (c) and Zn (d) concentrations in humus effluent, the experimental control and effluent treated with either FeCl₃ or Floculan (Mean \pm 95% CI).

In CF with FeCl₃ a sizeable amount of DOC (42%) was removed (Table 5.1). Therefore, despite the ability to remove modest amounts of soluble Cu (51%), Pb (54%) and Zn (31%) from effluent (Table 5.1), no significant reduction was observed in the bioavailable metal concentration following treatment as shown in Figure 5.3 panels a, b and d, respectively ($p > 0.05$). These findings indicate that FeCl₃ had no environmental benefit with regards to the toxicity of metals in effluent. Furthermore, an increase in the concentration of Ni coupled with DOC removal significantly increased the bioavailability of Ni in effluent treated with FeCl₃ ($p < 0.001$; Figure 5.3c). Based on these results CF with FeCl₃ may not be recommended for application in wastewater treatment for the removal of trace metals from municipal wastewater.

The pH of effluent is also a component input into BLMs. Nevertheless, the difference in the pH of effluent treated with FeCl_3 and Flocculant was not substantial (see Table 5.1) and was therefore unlikely to have significantly influenced the bioavailability of the residual metal.

5.3.6 Characterisation of flocs

5.3.6.1 Structural characteristics

Features observed in Figure A.1 were representative of FeCl_3 (0.81 FDM library match score). On the other hand, the spectrum generated for Flocculant (see Figure 5.4a) showed bands representative of organic compounds. Peaks were assigned in accordance with their respective wavenumbers (cm^{-1}) as reported in literature. A broad stretching peak around 3010 cm^{-1} was a combined effect of O-H and N-H groups (Hameed et al. 2016). The occurrence of stretching vibrations over a broad range of frequencies indicated the presence of bonded O-H bands of carboxylic acids and free hydroxyl groups (Gnanasambandam and Proctor, 2000). Peaks at 1599 and 1458 cm^{-1} indicated the presence of asymmetric and symmetric stretching vibrations of ionic carboxylic groups (COO^-) (Iqbal et al. 2009). The aliphatic acid group vibration at 1227 cm^{-1} can be assigned to deformation vibration of C=O and stretching formation of O-H groups of carboxylic acids and phenols (Guibaud et al. 2003). The effect of bending of C-O group was shown at the peak 1092 cm^{-1} (Hameed et al. 2016). It is well indicated from FTIR spectrum of Flocculant that hydroxyl, carboxyl and amino groups were present and, such groups, could be involved in coordination with metal ions.

Figure 5.4 also includes the FTIR spectra of suspended solids from the humus effluent and flocs produced after CF treatment. The spectra of the suspended solids from humus effluent (see Figure 5.4b) exhibited a broad band at 3254 cm^{-1} which represents O-H functional groups and O-H stretching of polymeric compounds. Major bands at the wavelengths 2979 and 2888 cm^{-1} correspond to C-H bonds of aliphatic acids (Farinella et al. 2007). The band at 1645 cm^{-1} corresponds to the C=C stretching that is associated with C-C bonds and COO^- asymmetric stretching's (Farinella et al. 2007). The peak at 1387 cm^{-1} represents aliphatic group vibration and COO^- symmetric stretching (Pavia et

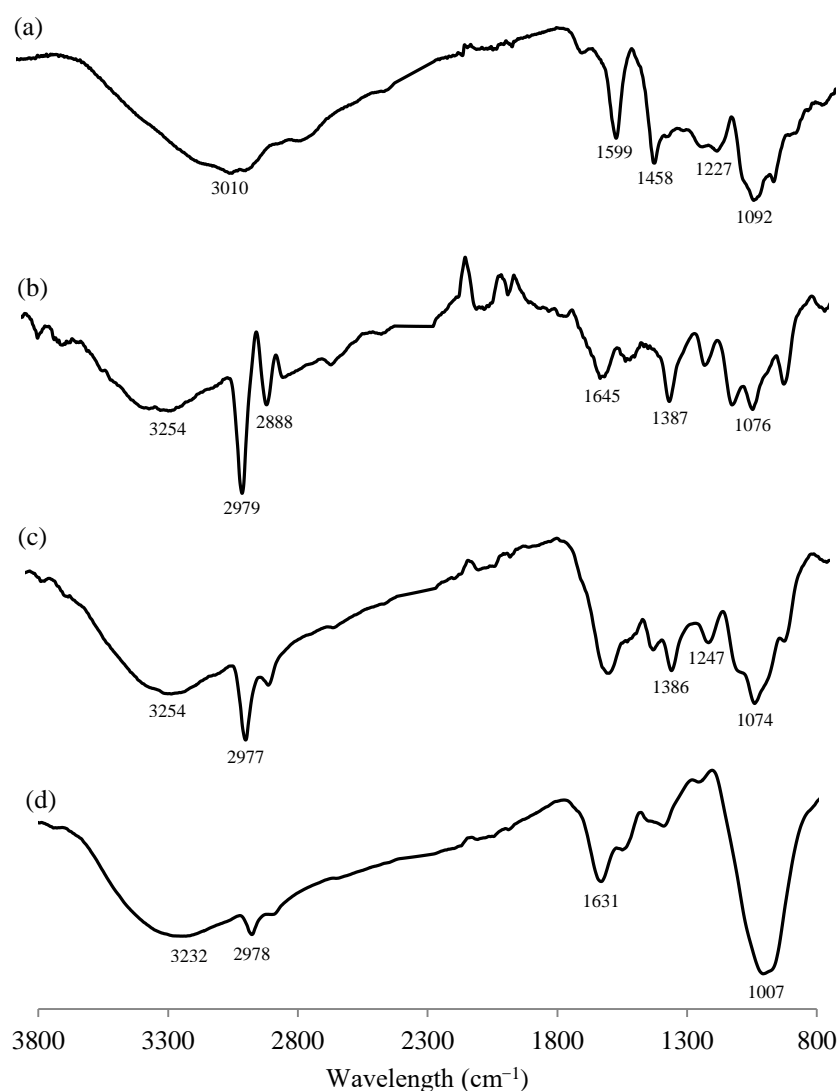


Figure 5.4 FTIR spectra of Floculan (a), suspended solids from humus effluent (b), and flocs produced by CF treatment using Floculan (c) and FeCl_3 (d).

al. 1996), whilst the band at 1076 cm^{-1} is indicative of the C-O group (Farinella et al. 2007).

The FTIR spectrum for flocs formed by Floculan (see Figure 5.4c) shared similar peak locations with the dried humus effluent suspension (Figure 5.4a), with bands around 3254 , 2979 , 1387 and 1076 cm^{-1} observed in both spectra. Such findings indicate that the polymeric chains within this reagent were capable of bridging organic molecules present in humus effluent together, incorporating them in flocs formed. Although Floculan contributed to the spectrum, introducing the peak which appeared at 1247 cm^{-1}

(carboxylic acids and phenols), the spectrum, overall, appears representative of the material collected from the humus effluent. This is not surprising, given that Flocculan itself (Figure 5.4a) has similar structural characteristics compared with the dried humus effluent suspension (Figure 5.4c).

Conversely, the FTIR spectrum for flocs produced by FeCl_3 (see Figure 5.4d) was strongly affected by this coagulant's chemistry. Reduced intensity of the peak around 2979 and 2888 cm^{-1} indicated suppression of non-charged components. In addition, peaks at 3254 , 1645 and 1076 cm^{-1} shifted to 3232 , 1631 and 1007 cm^{-1} , respectively. These shifts may be attributed to adsorbed carbohydrates or polysaccharide-like constituents (Gu et al. 1994); this indicates that complexation between C-O functional groups of suspended humus effluent particles and the surface of ferric hydroxide precipitates occurred. Hence, the removal of particles in a growing hydroxide precipitate, known as sweep flocculation (Duan and Gregory, 2003), played an important role in the CF process with FeCl_3 .

5.3.6.2 Morphological properties

From the SEM micrographs shown in Figure 5.5 it can be seen that the flocs produced after the treatment of humus effluent with either FeCl_3 (Figure 5.5a) or Flocculan (Figure 5.5b) were compact and clustered, indicating the presence of aggregates formed through the CF of particles by these reagents. In comparison, flocs which were formed by Flocculan exhibited a more compact structure with a smoother surface as a result of the formation of larger, denser and easier settling flocs. These characteristics are typical of flocs produced in CF with biopolymers through interparticle bridging, and are desirable for good settling and dewatering (Liao et al. 2006) and the formation of a low volume of sludge. Other studies (Renault et al. 2009) have revealed that metal salts hydrolyse rapidly when added to wastewater, producing abundant sludge that is difficult to dehydrate. Hence, explaining the **visibly** lower floc density observed for FeCl_3 in Figure 5.5b.

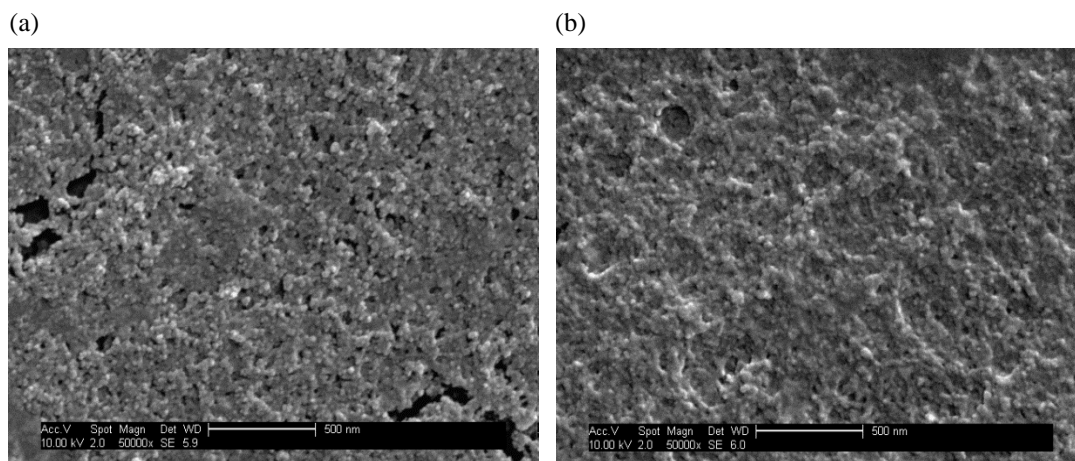


Figure 5.5 SEM images of flocs produced by CF treatment using FeCl_3 (a) and Flocculan (b).

5.4 Conclusions

This study was one of the first of its kind to assess the influence of CF on metal size distribution and bioavailability. The experimental findings herein indicate that CF with either FeCl_3 or Flocculan can simultaneously remove particulate and soluble metal from wastewater. In the CF process, both FeCl_3 and Flocculan removed Cu and Zn from the colloidal fraction in conjunction with the elimination of COC. Such findings indicate that technologies capable of removing organic materials within the colloidal fraction can reduce the concentration of Cu and Zn in effluent. Despite FeCl_3 achieving a higher rate of removal for COC, a significantly lower Cu concentration was observed in the colloidal fraction of effluent treated with Flocculan. It was anticipated that Flocculan removed organic compounds (such as polysaccharides and proteins) with functional groups that Cu readily complexes with. Furthermore, Flocculan removed Cu from the truly dissolved fraction through the complexation of Cu ions with functional groups (phenol and amino groups) present in the polymeric chains. This additional removal mechanism helped Flocculan outperformed FeCl_3 in the removal of soluble Cu. The bioavailability of metals in effluent was strongly influenced by the concentration of DOC. Flocculan was able to remove soluble Cu, Pb and Zn without reducing the concentration of DOC, thus was capable of simultaneously reducing the concentration and bioavailability of these metals in treated effluent. Flocculan should, therefore, be considered for its environmental benefits in decision making on municipal wastewater treatment. In CF with FeCl_3 a substantial amount of DOC was removed, therefore

despite achieving modest rates of removal for Cu, Pb and Zn, FeCl₃ did not reduce the bioavailability of target metals in treated effluent. Such findings suggest that failure to account for the effect of treatment technologies on DOC may result in the application of a technique which reduces metal concentrations in effluent discharges, but which does not deliver any environmental benefit. The CF performance data and proposed mechanisms of metals removal (i.e. sweep flocculation for FeCl₃; inter-particle bridging for Flocculan) were further supported by analysis of flocs formed, which included FTIR and SEM.

5.5 References

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Chapter 6

Discussion

6. Discussion

This chapter discusses the key findings of the research described in the preceding chapters in a broader perspective.

This research has shown that Flocculant can reduce concentrations of trace metals present in wastewater, with similar or better removal rates than that achieved with the conventional reagent, ferric chloride (FeCl_3) (Chapters 4, 5). Removal efficiency is, nonetheless, only a single criterion against which Flocculant's efficacy might be assessed and wastewater treatment works (WWTWs) operators will want to consider other factors. For example, the reagent should be obtainable from a sustainable source, and be able to compete effectively on both a cost and performance basis with other technologies. The first part of this chapter describes a number of important considerations concerning the environmental and financial suitability of Flocculant as a treatment option to enhance metals removal at WWTWs in the United Kingdom (UK).

This research has also shown that in effluent a substantial proportion of metal can be associated with colloidal materials (Chapters 3, 5). Current biotic ligand models (BLMs) assume complexation with humic substances (HSs) is the sole mechanism mitigating the toxicity of soluble metals. The second part of this chapter therefore considers the importance of accounting for colloiddally associated metal when assessing metal bioavailability.

6.1 Sustainability of Flocculant

6.1.1 Environmental sustainability

Aluminium (Al) and iron (Fe) salts are mass produced and can effectively remove a broad range of pollutants, thus are widely used as coagulants in water and wastewater treatment processes (Duan and Gregory, 2003). Nevertheless, life cycle assessments of water and WWTWs that use metal salts have revealed that coagulant production carries a significant environmental burden (Vince et al. 2008; McNamara et al. 2016; Niero et al. 2014). This is mainly due to the energy requirements of the chemical production process and the emissions released (Vince et al. 2008). FeCl_3 is industrially produced by direct chlorination which involves a high temperature reaction of scrap iron with dry

chlorine (European Commission [EC], 2005) that generates large amounts of greenhouse gas emissions and releases pollutants such as manganese and mercury (Vince et al. 2008; Niero et al. 2014). Gaseous emissions also include tetrochloromethane which depletes the ozone layer (Vince et al. 2008). To produce Al salts, Bauxite is mined from topsoil and is then chemically transformed to extract Al and produce industrial materials. This requires significant amounts of energy, and the use of fuel, water and reagents (Norgate et al. 2007) and thus also contributes to resource depletion and greenhouse gas emissions. These impacts are undesirable and may be reduced by using alternative reagents.

In recent years, efforts have been made to investigate the usefulness of natural coagulants for the treatment of wastewater, in particular, coagulants derived from plants and which are freely available from farm and forest resources (Saranya et al. 2014). Although a variety of plant-based coagulants have been reported in the scientific literature, two main types have been studied extensively by the research community, namely, seeds from *Moringa oleifera* and tannin. *Moringa oleifera* (drumstick or horseradish tree) is a tropical plant found in Latin America, Asia and sub-Saharan Africa (Jahn, 1988; Sanghi et al. 2002). The seeds contain positively charged, water-soluble proteins that aggregate particles through adsorption and charge neutralisation mechanisms (Ndabigengesere et al. 1995). Indeed, studies have found that when using seeds from *Moringa oleifera* trees in the coagulation-flocculation (CF) process, similar or better performance can be achieved compared with conventional metal salts (Ndabigengesere et al. 1995). Encouraged by such results, the cultivation and usage of this plant as a natural coagulant is currently being promoted in many developing countries (Shan et al. 2017). However, natural limitations in the supply of its seeds has restricted further commercialisation and, hence, broader deployment (Kansal and Kumari, 2014).

On the contrary, Tannin, defined as large polyphenol compounds, can be extracted from vegetal secondary metabolites including bark, fruits and leaves from *Acacia*, *Castanea* and *Schinopsis*, whilst non-tropical species such as *Quercus ilex*, *ruber* and *suber* also have bark rich in tannin (Beltrán Heredia and Sánchez Martín, 2009). As these are widely spread and the tannin extraction process relatively straightforward (Choy et al.

2014), tannins have been successfully commercialised as a water and wastewater treatment technology and are available in a number of different water treatment product formulations such as Ecotan (Servyeco Group, Spain), Floccotan (Floccotan (Pty) Ltd, South Africa) and Tanfloc.

A trademark of TANAC (Brazil), Tanfloc is composed of tannin obtained from *Acacia mearnsii* bark. TANAC operates a forest management practise that is certified by the Forest Stewardship Council (FSC), which checks companies against a set of principles, criteria and indicators to assess whether management is socially beneficial, economically viable and environmentally appropriate (World Wide Fund for Nature [WWF], 1994). TANAC operates a unique reforestation system; up to 7 million *Acacia mearnsii* trees are planted each year and continue to grow during a seven year cycle. The tannin extraction process is reported by dos Santos Grasell et al. (2016) and is summarised below.

Aqueous extraction of tannins from ground bark occurs without the use of any solvent, and exhausted bark that passes through the autoclaving process is pressed and the water recycled in the next extraction. Exhausted pressed bark and any secondary wood is used as a biofuel in the steam boilers that provide power to the site, without the need for external non-renewable sources. In addition, any excess bark (< 1%) is used in organic compost thus the whole of the *Accacia mearnsii* trees are used avoiding the generation of any waste. Tannin extraction is therefore considered to be sustainably managed.

Extracted tannins can be traded in liquid form, as a powder (after atomisation) or as a solid block (after evaporation) (dos Santos Grasell et al. 2016). The extracted liquid can also undergo chemical modification to produce Tanfloc. The process is relatively straightforward (Beltrán Heredia and Sánchez Martin, 2009) and involves, (1) reaction of an ammonium salt with an aldehyde, and, (2) reaction of this complex mixture with tannin, forming a polyelectrocatyltic cation (Lamb and Decusati, 2002). Tanfloc has been commercially available in Brazil for more than 30 years and an effective distribution network is in place, as Tanfloc is currently exported to ~20 countries worldwide (TANAC, 2015). In the UK, Flocculan, an aqueous solution which contains up to 30% Tanfloc is commercially available as a wastewater treatment technology (Lansdowne Aquatec, UK). Flocculan can be used to increase the concentration of solids

in mechanical dewatering processes, to thicken primary sludge and to treat industrial effluents. Flocculant may also be used alone or in conjunction with traditional coagulants in the drinking water treatment process (Lansdowne Aquatec, 2017). Given that tannins can be sustainably managed and industry is in a position to respond to new demand, Flocculant could be viewed as favourable for development and promotion as a treatment option for sustainable metal management at municipal WWTWs in the UK.

6.1.2 Financial sustainability

Cost is an important aspect for consideration when selecting the processes and substances to be deployed in wastewater treatment. Despite its commercial availability, the unit price of Flocculant (£0.65/kg, Lansdowne Aquatec, A. Lee 2017, personal communication) is substantially higher than that of FeCl_3 (£0.16/kg, Nexchem, A. Major 2017, personal communication). An observation from this research (Chapter 4) was that for the optimum removal of target metals from effluent, larger amounts of Flocculant (0.25 mg/L) were required compared with FeCl_3 (0.10 mg/L). With the prices stated above, and assuming that 0.25 mg/L of Flocculant and 0.10 mg/L of FeCl_3 are used to treat the same volume of effluent, it is estimated that it would cost around ten times more to use Flocculant in the CF process compared with FeCl_3 (Table B.1). Although Flocculant appears expensive, it is important to recognise that these cost values do not take into account how an increase in demand might reduce the unit price of Flocculant, so this comparison of costs is likely to be conservative. In addition, calculated costs do not consider the chemical cost of pH adjustment typically required in CF with metal salts (Saranya et al. 2014). A treatment works configuration that does not require pH adjustment is, therefore, desired for system simplicity and to lower treatment costs (Pepin et al. 2003). It is not necessary for Flocculant to be hydrolysed in effluent to neutralise the charges of particulates and colloidal matter, therefore this reagent does not alter the pH of treated wastewater (Chapters 4, 5).

Moreover, the cost of sludge handling is expected to create large differences in overall treatment costs. In the CF process, the production of sludge is a significant challenge faced at treatment facilities and is of particular importance because sludge treatment and disposal can account for up to 60% of total operating costs at WWTWs (Teh et al. 2016). Sludge generated must be dewatered after the treatment process (Chaudhari et al.

2010; Verma et al. 2010), which will incur additional costs as a separate unit for sludge handling is generally required (Teh et al. 2016). In order to reduce the costs associated with sludge the most obvious solution is to minimise its generation within the treatment process. Inorganic Fe and Al salts hydrolyse rapidly in wastewater, generating large volumes of sludge which is difficult to dehydrate (Renault et al. 2009) whereas the polymers contained within Flocculan aggregate particles by the mechanism of inter-particle bridging which produces compact flocs with smooth surfaces (Shak and Wu, 2014; Teh et al. 2014; Chapters 4, 5); characteristics desirable for efficient settling, dewatering and the production of low sludge volume (Liao et al. 2006). For example, Haydar et al. (2009) found that treatment with the cationic polymer C-496 produced 65% less sludge volume compared with Al sulphate (alum). Amuda and Amoo (2007) found that when using FeCl_3 in combination with polyacrylamide for the treatment of industrial (beverage) wastewater, a 60% reduction in sludge was obtained compared with using FeCl_3 alone. In a study by Ndbigengessre et al. (1995), the volume of sludge produced in CF with *Moringa oleifera* was approximately 4-5 times lower than that produced by alum coagulation. Furthermore, studies have revealed that sludges formed by tannin based coagulants (including Tanfloc) are less voluminous and have better permeability than sludges formed by conventional metal salts (Özacar and Şengil, 2000; Aboulhassan et al. 2016; Hameed et al. 2016).

6.1.3 Sludge management

The value of converting sludge generated by the CF process into a useful by-product is also an important concept to be considered by WWTWs operators. However, the use of metal salts in the CF process increases the toxicity potential of the generated sludge which prevents or limits its reuse (Renault et al. 2009). For example, consumption of Al species may lead to Alzheimer's disease (Dassanayake et al. 2015), whilst Al in soil tends to fix phosphorous preventing its assimilation in the roots of plants (Vanacôr and Gehling, 2007). As a result of the formation of reactive oxygen species, Fe is both a nutrient and a toxin to microorganisms (De Freitas and Meneghini, 2001). Thus, application of sludge containing Fe to land may be advantageous as it can improve nutritional value, but must be carefully monitored. In contrast, biopolymers generate biodegradable and non-toxic sludge which can be efficiently degraded by

microorganisms (Renault et al. 2009) and may be reused for agricultural application (Teh et al. 2014; Shak and Wu, 2015). For example, Vanacôr and Gehling (2007) investigated the quality of sludge produced from a conventional water treatment plant (Porto Algre, Brazil) when treated with Tanfloc, and revealed that sludge generated was disposable in soil where it was stable for agricultural use. In fact, other studies (Medtler and Miranda, 2011) have proposed that Tanfloc may even improve the physio-chemical characteristics of soil, owing to its organic composition. Nevertheless, some researchers (Zhou et al. 2008) strongly recommended that sludge should not be re-used as fertilisers due to the presence of residual metals in the dewatered sludge. This highlights that, before its application to land, the environmental impact of sludge generated by a prospective reagent must be addressed.

The present study is the first to report data on the use of Flocculan to remove trace metals from municipal wastewater and the practicalities of sludge production and management when using this agent have yet to be explored. This is a key area that could be addressed in future work to ascertain whether Flocculan can achieve and sustain comparable (or reduced) treatment costs in comparison with established chemical coagulants (see section 7.3, Future work).

6.2 Bioavailability and the Biotic Ligand Model approach

BLMs convert a dissolved phase metal concentration to an equivalent bioavailable metal concentration (and vice versa) by simulating the influence of site-specific physico-chemical characteristics (pH, hardness, dissolved organic carbon [DOC]) on metal bioavailability (Di Toro et al. 2001; Peters et al. 2009). When simulating interactions of metals with these parameters the models assume that DOC is composed of HSs, which are known to be responsible for complexing a variety of metal ions in natural waters (Reuter and Perdue, 1977; Higgs et al. 1993; Christl et al. 2001; Tipping, 2002). HSs are defined as natural macromolecular polymers which have irregular, heterogeneous structure (MacCarthy and Rice, 1991), and are known to comprise a substantial proportion (50-90%) of surface water DOC (Thurman, 1985). Although the accuracy of BLMs has been verified in a variety of natural waters, the effectiveness of BLM forecasts when applied to effluent impacted waters is, however, less certain. The proportion of effluent that might be considered to be HSs is much smaller than in river

waters. For example Imai et al. (2002), who studied several treatment facilities operating different treatment types, revealed that HSs contributed from 3-28% of effluent DOC. Studies on the characterisation of effluent organic matter have revealed the presence of non-humic macromolecules including polysaccharides and proteins (Jarusutthirak et al. 2002; Shon et al. 2006; Nam and Amy, 2008; Wang and Wu, 2009) to which metals may adsorb or complex with (Pernet-coudrier et al. 2008; Sheng et al. 2013). In fact, several studies (Baken et al. 2011; Louis et al. 2014; Constantino et al. 2015) have found that within effluent and anthropogenically impacted waters a category of non-humic ligand may exist that binds strongly with metal ions. Such findings have led to the proposition that non-humic ligands should be included as an additional category within BLMs (Constantino et al. 2015).

Whereas the present study did not examine effluent derived ligands and the extent to which these might influence a metal's chemical form (speciation), this study has identified a substantial colloidal fraction in effluent that might indeed influence metal speciation (Chapters 3, 5). BLMs do not specifically account for the influence of colloids (these may not be particularly important for river waters that are not significantly impacted by effluent discharges), suggesting that current BLMs may be over-simplified since these assume that complexation with HSs is the only mechanism mitigating the toxicity of soluble phase metals. This simplification may result in an overestimation of the bioavailable metal concentration, that might ultimately lead to a requirement to reduce metal concentrations in effluent, but which delivers no environmental benefit (Constantino et al. 2015). This is of particular importance in the UK and regions of North America which have low effluent dilution capacity ($\leq 1:10$; Keller et al. 2006) and that use the BLM approach for regulatory purposes (Chapter 2). Hence, findings from this study support the case for considering the influence of colloids (not only complexation) when assessing metal bioavailability and toxicity, and for determining compliance with bioavailability-based standards.

6.3 Future research

During this project further areas of research have been identified, these are listed below:

- The coagulation-flocculation trials described in this thesis were conducted at bench-scale, and succeeded in establishing the effectiveness of Flocculan for trace metal removal from municipal wastewater (Chapters 4, 5). However, the findings of this research must be scaled up, to verify the findings at pilot scale or at a small, full-scale WWTWs. The practicalities of operation, such as sludge production and management, need to be further investigated to enable a well-rounded business case for the implementation of Flocculan as a metal management option in the wastewater sector to be developed.
- Although this research succeeded in determining the size distribution of metals at a full-scale WWTWs (Chapters 3, 5) the composition of influent is expected to vary between works, particularly for parameters such as DOC, which are influential in soluble metal fractionation. Therefore to understand if the observed size distribution of metals at the site investigated is unique, or broadly representative of other sites operating in the UK, further investigations into the distribution of metal (i.e. particulate, colloidal, truly dissolved) in influents and effluents at other WWTWs is required. It would be recommended to characterise influent and effluent at sites operating different treatment configurations (e.g. trickling filters, activated sludge) to account for changes in metal fractionation that might occur as a result of treatment type.
- In effluent, a substantial proportion of metal was distributed in the colloidal fraction (Chapters 3, 5). It is important to understand if metal in effluent remains bound in the colloidal fraction after mixing with river waters and if colloiddally bound metal species mitigate metal toxicity by limiting the transport of potentially toxic metals through the aquatic food web in receiving waters. Hence, findings from such work would have important implications for our understanding of metal-related risk.

6.4 References

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Chapter 7

Mercury and Antimony in Wastewater: Fate and Treatment

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7. Mercury and Antimony in Wastewater: Fate and Treatment

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Abstract

It is important to understand the fate of mercury (Hg) and antimony (Sb) within the wastewater treatment process so as to examine potential treatment options and to ensure compliance with regulatory standards. The fate of Hg and Sb was investigated for an activated sludge process treatment works in the United Kingdom. Relatively high influent values (Hg: 0.09 µg/L, Sb: 1.7 µg/L) were observed at the works, whilst low removal rates within the primary (Hg: 52%, Sb: 16%) and secondary treatment stages (Hg: 30%, Sb: -29%) resulted in final effluent concentrations of 0.03 µg/L for Hg and 2 µg/L for Sb. Removal of Hg was positively correlated with suspended solids and chemical oxygen demand removal, whilst Sb was negatively correlated. Elevated final effluent Sb concentrations compared with influent values were postulated and were suggested to result from Sb present in returned sludge liquors. Kepner Tregoe analysis was applied to identify suitable treatment technologies. For Hg, chemical techniques (specifically precipitation) were found to be the most suitable whilst for Sb, adsorption (using granulated ferric hydroxide) was deemed most appropriate. Operational solutions, such as lengthening hydraulic retention time, and treatment technologies deployed on sludge liquors were also reviewed but were not feasible for implementation at the works.

7.1 Introduction

Wastewater treatment works (WWTWs) receive metal inputs from both domestic and industrial sources, therefore discharges from WWTWs have the capacity to elevate metal concentrations in rivers such that harm may occur (Stumm and Morgan, 2012). Whereas metals such as copper (Cu) and zinc (Zn) have been the subject of numerous studies (Chipasa, 2003; Beck and Birch, 2012; El Khatib et al. 2012) trace metals such as mercury (Hg) and antimony (Sb) are not monitored on a regular basis (Choubert et al. 2011). Nevertheless, they have been observed throughout the various stages of the wastewater treatment process (Yoshida et al. 2013).

There are strong regulatory drivers that require Hg and Sb removal as part of the wastewater treatment process. Hg is classified as a Priority Hazardous Substance (PHS) under the Water Framework Directive (WFD) (2000/60/EC) requiring emission cessation. The WFD currently requires that Hg concentrations do not exceed 0.05 µg/L as an annual average (AA) and 0.07 µg/L as a maximum allowable concentration (MAC) in inland surface waters. In the United States (US), in accordance with the Clean Water Act (1972), national recommended Water Quality Criteria outline standards for the protection of aquatic life and human health in surface water. For Hg the criterion continuous concentration (CCC) is 0.77 µg/L and the criteria maximum concentration (CMC) is 1.4 µg/L, whilst Sb concentrations may not exceed 5.6 µg/L.

In the United Kingdom (UK) the concentration of Sb in drinking water may not exceed 5 µg/L (Department for Environment, Food and Rural Affairs [DEFRA], 2015). A combination of factors such as low effluent dilution capacity and that drinking water abstraction locations are often located downstream of WWTW discharges, mean WWTWs operators seek to reduce the concentration of Sb in effluent.

Hg enters wastewater from a variety of sources including dental practice wastes, which can contribute up to 50% influent Hg concentrations (Bender, 2008), fertilizers, landfill leachate, paints, domestic waste inputs, groundwater infiltration, stormwater drainage contributions and historical sources of Hg (Wang et al. 2004; Gbondo-Tugbawa et al. 2010). External and tankered sludge inputs have also been found to influence metal concentrations within the wastewater treatment process potentially increasing metal

content, including Hg, within final effluent discharges (Grady Jr. et al. 2012). Sb concentrations at WWTWs are predominantly associated with its use as a flame retardant in consumer electronics (van Velzen et al. 1998). Other sources of Sb include paints and landfill leachate, which Cyr et al. (1987) reported may contain concentrations in the region of 10 µg/L.

Although there is a need to enhance the removal of these pollutants, an understanding of their fate within WWTWs is limited (Rogers, 1996). Indeed, studies into the fate of Sb within WWTWs are rare and existing data focuses on Sb behaviour within natural aquatic systems (Fillela et al. 2002). Although the concentrations of Hg in influent and effluent as well as treatment process removal rates have been assessed (Goldstone and Lester, 1991; Rule et al. 2006), Hg fate throughout WWTWs is seldom discussed.

Some information on technologies that may be suitable to treat these metals is available. Physico-chemical techniques have been considered as potential treatment options (Guo et al. 2009; Ungureanu et al. 2015), whilst membrane filtration has also been deployed for Hg and Sb removal (Chiarle et al. 2000; Kang et al. 2000). The feasibility of specific technologies has not, however, been assessed in the context of future metal management at WWTWs.

This study assess the fate of Hg and Sb and examines the influence of different treatment stages on the overall removal rates at a WWTWs. Operational solutions, such as lengthening sludge retention time (SRT), and technologies available for Hg and Sb treatment are also reviewed.

7.2 Material and methods

7.2.1 Study site

The WWTWs examined in this study is located in the UK and utilises the activated sludge (AS) treatment technology. The site receives wastewater from a large urban catchment population. The site also accepts external site sludge inputs and domestic waste contributions. A schematic diagram showing the arrangement of treatment processes at the site is provided in Figure 7.1.

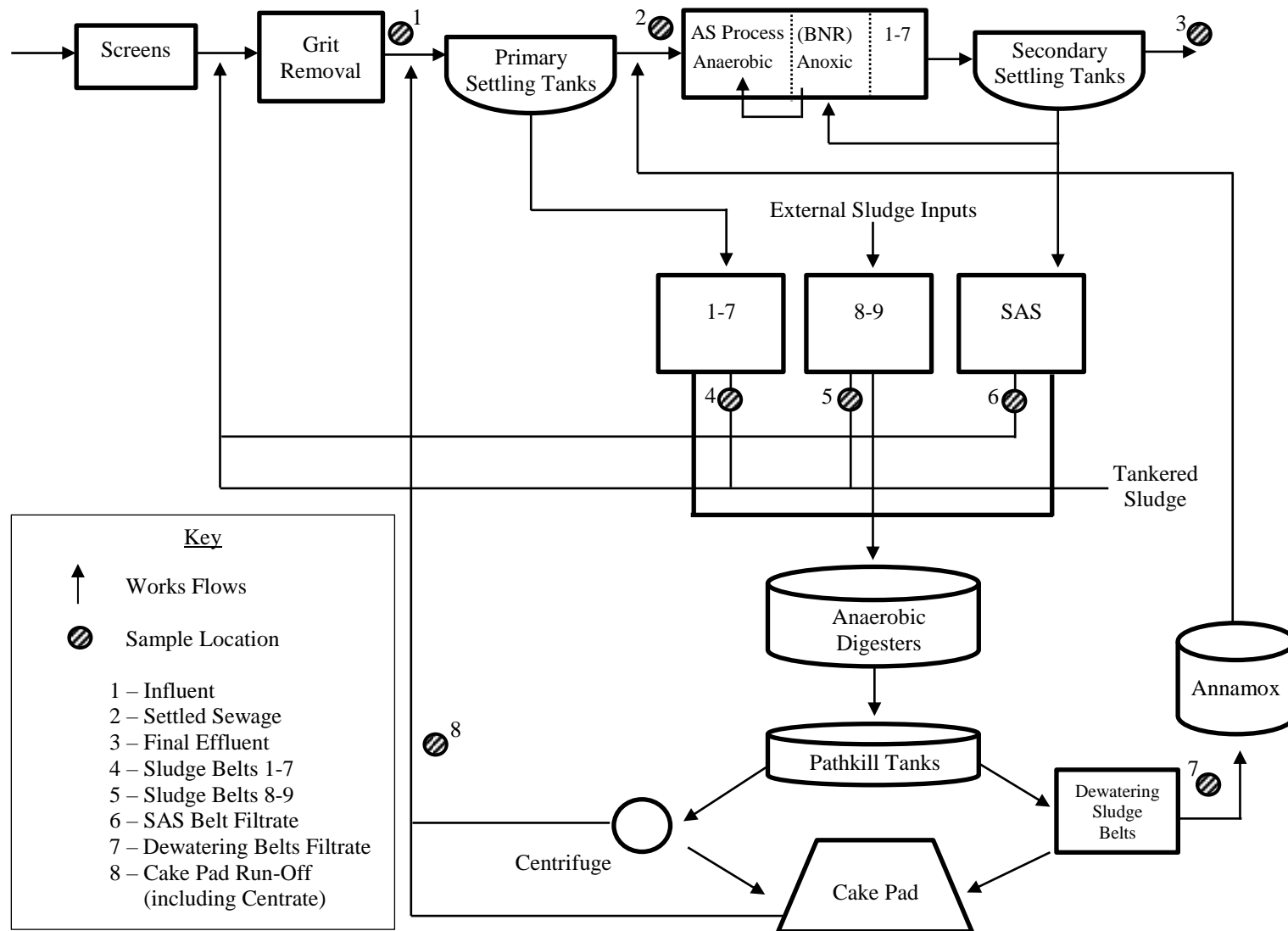


Figure 7.1 Simplified flow sheet for the site studied including sample locations.

Influent is initially subject to screening and grit removal processes. Wastewater is treated within primary settling tanks followed by AS treatment, consisting of seven lines which operate in a biological nutrient removal (BNR) configuration (containing anaerobic, anoxic, and oxic phases). Primary and secondary sludge are thickened separately on sludge belts 1-7 and the surplus activated sludge (SAS) belt respectively. Whilst external sludge inputs enter sludge belts 8-9. Sludge is then treated using anaerobic digestion and is moved into pathkill (secondary digestion) tanks, after which the sludge is dewatered and stored on a cake pad.

7.2.2 Sample collection

Hg and Sb concentrations were measured across the works from November 2013 to March 2015 at a number of treatment stages identified in Figure 7.1, namely; influent (1), settled sewage (2), final effluent (3), sludge belts 1-7 (4) and 8-9 (5), SAS belt filtrate (6) dewatering belts filtrate (7) and cake pad run-off (including centrate) (8). A minimum of four grab samples were taken from each location every month. Settled sewage and SAS belt filtrate samples were collected intermittently.

7.2.3 Analytical methods

Using standard vacuum filtration equipment and following American Public Health Association (APHA) (2005) procedures concentrations of total suspended solids (TSS) were determined, whilst total chemical oxygen demand (COD), phosphate (PO_4) and ammonical nitrogen (NH_4) concentrations were determined using cell test kits (Fisher Scientific, Leicestershire, UK Ltd). After acidification with nitric acid (HNO_3), samples were analysed for Hg and Sb content using an ELAN 9000 inductively coupled plasma-mass spectrometer (ICP-MS) (Perkin Elmer, Beaconsfield, UK).

7.2.4 Data analysis

Removal of TSS, COD, PO_4 and NH_4 was calculated at each treatment stage and throughout the works as a whole. Analysis of these sanitary determinands was undertaken to ensure that the treatment works was operating as expected. Overall and individual treatment stage removal rates were also calculated for Hg and Sb. The dataset was collated into seasonal periods comprising of spring (March, April, May), summer

(June, July, August), autumn (September, October, November) and winter (December, January, February) to identify patterns in Hg and Sb inputs and/or works performance, and in particular, to assess the significance of metal mobilisation by rainfall on influent and effluent concentrations. One-Way ANOVA tests were used for statistical analysis which considered the significance, with the threshold $p < 0.05$, of year on Hg and Sb concentrations found throughout the works, whilst the influence of seasonality on removal rates and the effectiveness of treatment stages were also assessed. Pearson's correlation coefficient tests were used to identify trends between sanitary determinand and metal removal, and to identify if rainfall (using Met Office data) influenced Hg and Sb concentrations found in influent and effluent samples.

7.2.5 Kepner Tregoe analysis

The treatment technologies available to enhance the removal of Hg and Sb were identified from a review of literature with a screening process employed to select the candidate technologies. Screening involved the elimination of technologies unable to remove Hg and Sb to concentrations below UK (Hg: $< 0.05 \mu\text{g/L}$; Sb: $< 5 \mu\text{g/L}$) and US (Hg: $0.77 \mu\text{g/L}$; Sb: $5.6 \mu\text{g/L}$) standards. In order to evaluate the screened technologies and select the most suitable to remove Hg and Sb from wastewater a Kepner Tregoe (KT) analysis was undertaken (KT, 2013). KT is a decision making approach, which utilises selection indicators and assigned weightings, and incorporates a point scoring system enabling technologies to be compared in relation to their suitability. The selection indicators and weightings chosen (Table 7.1) represent the most important considerations for the wastewater treatment operator (based on feedback from wastewater treatment specialists, $n = 10$), with studies at WWTWs with equivalent research conditions (e.g. metal concentrations) utilised to inform treatment technology selection.

Table 7.1 KT selection indicators, their weightings and associated operational criteria.

Selection indicators	Operational criteria	Weighting
Effectiveness for concentration range	The technology can achieve by itself the final Hg and Sb requirements	10
Footprint	It is compact and/or can be retrofitted into the existing works	8
Capital expenditure (CAPEX)	Costs and feasibility of construction	6
Energy consumption	Energy requirements for technology usage	7
Maintenance requirements	Costs of continual operation	6
Chemical usage	Quantity, diversity and hazardous nature of chemical usage	5
Ready to use	Proven to work on wastewater at full scale anywhere in the world	5

7.3 Results

7.3.1 Works operating conditions

The calculated removal rates for NH_4 (100%), TSS (97%), COD (94%) and PO_4 (85%) indicated that the treatment works operating conditions were satisfactory (Table 7.2). Analysis of flow rate data also found that seasonality had no significant influence ($p = 0.453$) on inflows at the works. Therefore the average flow rate (507 610 m^3/d) was used within mass flux calculations (Figure 7.2).

Table 7.2 Removal rates observed at the works for Hg, Sb and sanitary determinands.

Removal Rate (%)	Hg	Sb	PO_4	NH_4	TSS	COD
Primary removal	52	16	28	96	47	59
Secondary removal	30	-29	79	99	94	84
Overall removal	66	-15	85	100	97	94

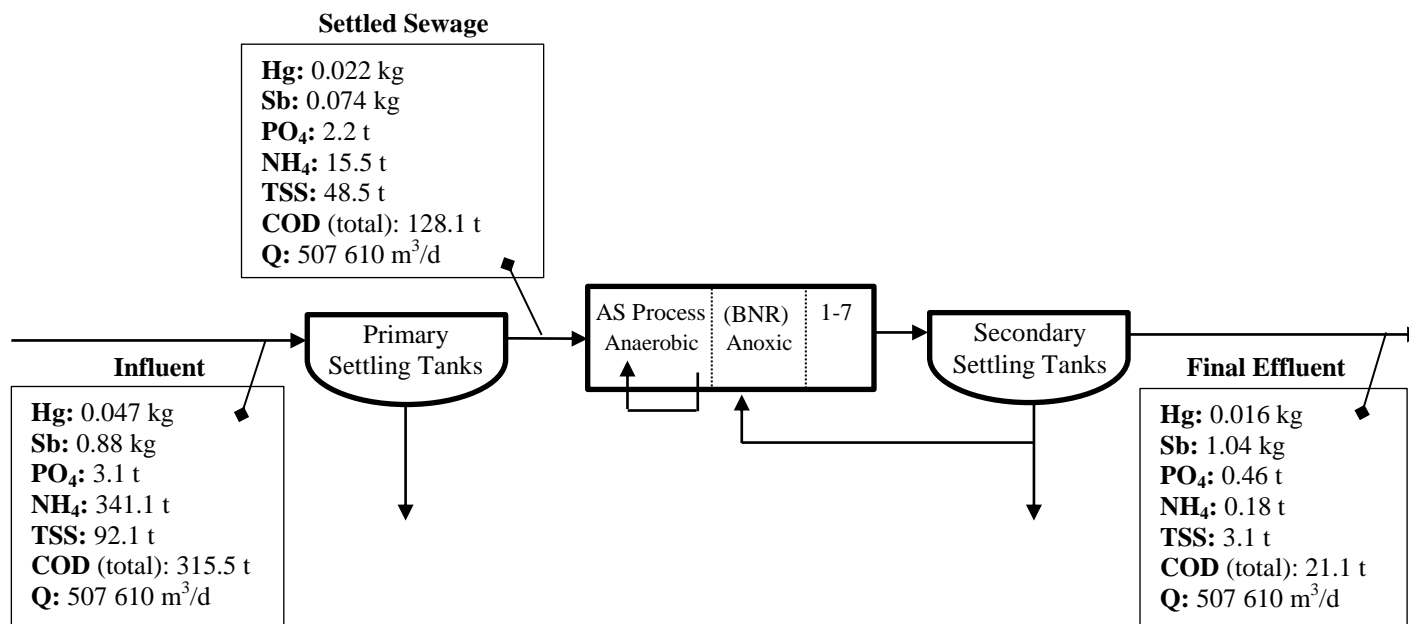


Figure 7.2 Mass flux calculated for the works.

7.3.2 Mercury and antimony removal

The overall rate of removal for Hg (66%) was low compared with values recorded for sanitary determinands (85-100%), with substantially lower Hg removal recorded for the secondary treatment stage (30%) in comparison with the primary treatment stage (52%). Concentrations recorded at sample locations 1-3 (Figure 7.1) for Hg at the works were not statistically significant ($p = 0.08$), with a small change between mean influent (0.09 µg/L) and final effluent values (0.03 µg/L) and little difference between mean settled sewage (0.04 µg/L) and final effluent concentrations (0.03 µg/L), which ranged from 0.01 µg/L to 0.06 µg/L. The final effluent concentrations were therefore below the current MAC-environmental quality standard (EQS) (0.07 µg/L) and AA-EQS (0.05 µg/L) (Figure 7.3a).

Mean concentrations of Hg within the cake pad run-off (1.3 µg/L) were high compared with sludge belts 1-7 (0.8 µg/L), sludge belts 8-9 (0.3 µg/L), SAS belt filtrate (0.4 µg/L) and dewatering belts filtrate (0.2 µg/L). However, the large variability of Hg concentrations observed for each sludge sample location at the works (Figure 7.3b) meant that the differences between sample points were not statistically significant ($p = 0.494$).

A significant positive correlation between TSS and Hg removal was observed for the works ($r = 0.514$; $p < 0.001$), with a statistically significant, albeit small, positive correlation between Hg and COD removal ($r = 0.189$; $p = 0.02$). These correlations confirm that removing TSS will improve Hg removal at the works.

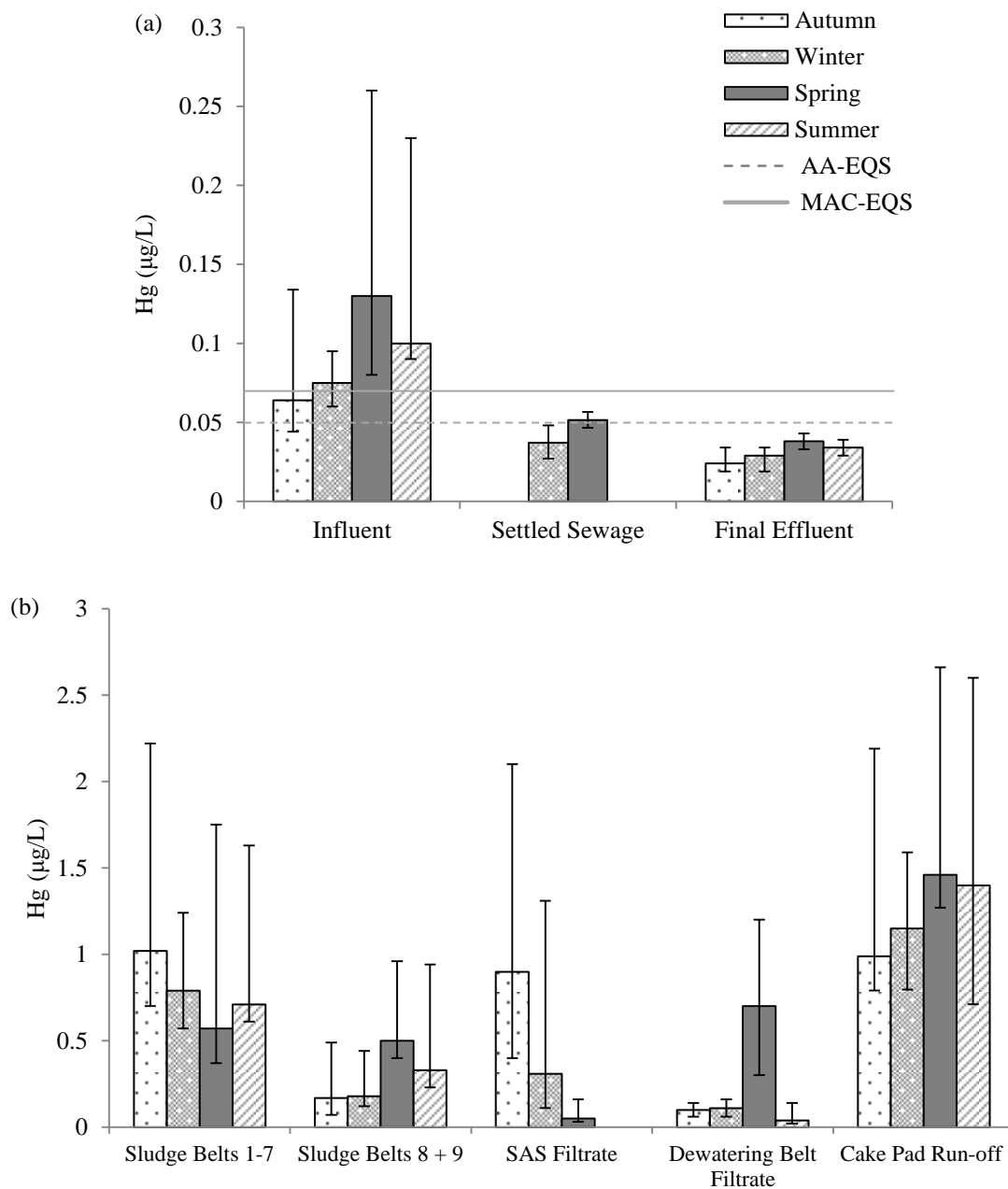


Figure 7.3 Hg concentrations observed in effluent (a) and sludge samples (b) at the works [Mean \pm standard deviation (SD)] in relation to the current AA-EQS and MAC-EQS.

For Sb, although some removal occurred at the primary treatment stage (16%), negative removal was recorded across secondary treatment (-29%) with an overall removal rate of -15%, indicating that Sb concentrations increased throughout the works. This observation was reflected within recorded concentrations which showed little change between influent (1.7 µg/L) and settled sewage values (1.5 µg/L), whilst Sb concentrations were enhanced in final effluent (2 µg/L) (Table 7.3). Differences

between these sample points were not statistically significant ($p = 0.217$). Furthermore, the coefficient of variation (CoV) demonstrates an increase in variability across the works treatment stages, similar values for influent (0.4) and settled sewage (0.4) were calculated whilst a substantially higher value was observed for final effluent (0.7).

Table 7.3 Sanitary determinand and metal concentrations observed in influent, settled sewage and final effluent samples at the works (Mean \pm SD).

Determinand	Influent	Settled Sewage	Final Effluent
SS (mg/L)	177.11 (79)	92.52 (32)	6.08 (1.5)
PO ₄ (mg/L)	5.93 (1.6)	4.26 (0.7)	0.91 (0.2)
NH ₄ (mg/L)	671.41 (264)	30.51 (8.22)	0.36 (0.4)
COD (mg/L)	621.61 (160)	252.41 (51)	40.02 (7.8)
Hg (μ g/L)	0.092 (0.06)	0.044 (0.03)	0.031 (0.03)
Sb (μ g/L)	1.73 (0.7)	1.45 (0.6)	2.04 (1.4)

Mean concentrations of Sb within sludge belts 1-7 (7.8 μ g/L) and sludge belts 8-9 (6 μ g/L) were high compared with SAS belt filtrate (3 μ g/L), dewatering belts filtrate (5.1 μ g/L) and cake pad run-off (5.1 μ g/L). However, the large variability of Sb concentrations observed for each sludge sample location at the works (Figure 7.4b) meant that the differences between sample points were not statistically significant ($p = 0.214$).

A statistically significant negative correlation was observed between Sb and TSS removal ($r = 0.653$; $p < 0.001$) as well as Sb and COD removal ($r = 0.545$; $p = 0.004$) at the works. These correlations demonstrated that removing SS and COD from the works had little effect on Sb removal.

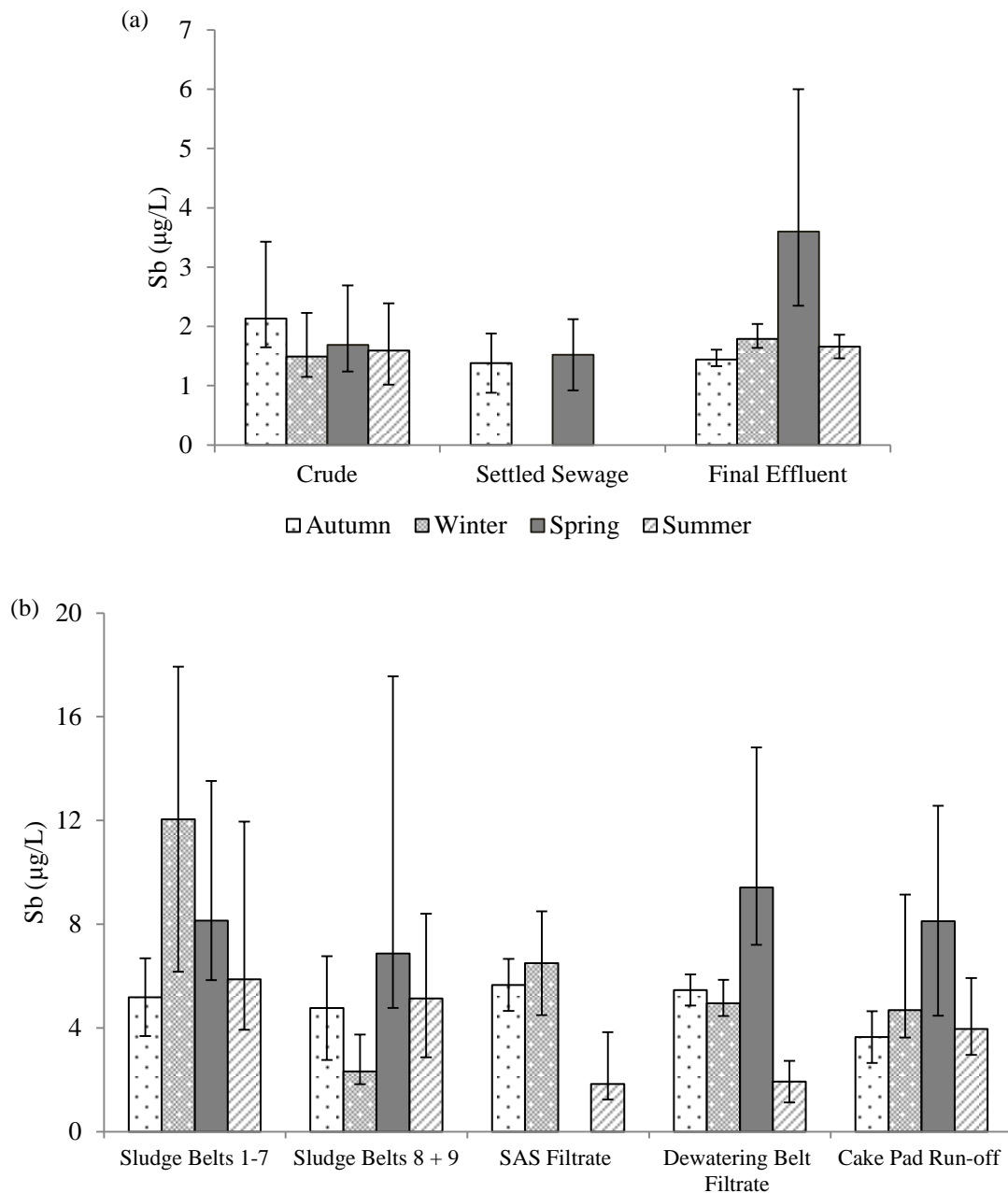


Figure 7.4 Sb concentrations observed in effluent (a) and sludge samples (b) at the works (Mean \pm SD).

7.3.3 Influence of seasonality on mercury and antimony concentrations

It was initially determined that year had no significant influence on Hg or Sb concentrations found within influent (Hg: $p = 0.225$; Sb: $p = 0.164$), effluent (Hg: $p = 0.358$; Sb: $p = 0.121$) and sludge samples (Hg: $p = 0.271$; Sb: $p = 0.103$). Justifying the collation of data into seasons for further analysis.

Differences in the mean, seasonal concentrations recorded at all sludge sample locations were not statistically significant for Hg ($p = 0.242$; Figure 7.3b) or Sb ($p = 0.191$; Figure 7.4b) at the works. Similarly, differences in the mean seasonal Hg concentrations recorded for influent, settled sewage and final effluent samples were not statistically significant ($p = 0.271$; Figure 7.3a). However, as demonstrated in Figure 7.4a, significant seasonal variation was present for Sb concentrations observed in final effluent ($p = 0.037$) with further analysis determining that spring Sb concentrations were higher than those recorded for other seasons.

No statistically significant correlation was observed between rainfall and Hg ($r = 0.09$; $p = 0.168$), and rainfall and Sb concentrations ($r = 0.06$; $p = 0.205$) observed within influent and final effluent samples, indicating that rainfall did not mobilise Hg or Sb into the works or influence the effectiveness of wastewater treatment.

7.3.4 Technology selection to enhance mercury and antimony removal

The initial screening process highlighted that membrane filtration, bioremediation, adsorption, chemical and ion exchange technologies (Table 7.4) could be used to remove Hg and Sb to below UK (Hg: 0.05 µg/L; Sb: 5 µg/L) and US (Hg: 0.77 µg/L; Sb: 5.6 µg/L) standards. The results of the KT analyses, which assessed the suitability of current effluent treatment technologies for implementation at the works, are presented in Figure 7.5. Chemical techniques were determined as most appropriate to enhance Hg removal at the works (Figure 7.5a) as this low cost option can treat large volumes of wastewater, is effective over a wide pH range and exhibits operation simplicity (Karman et al. 2015; Ungureanu et al. 2015). Adsorption was deemed most suitable to increase Sb removal (Figure 7.5b) as a variety of adsorbents have been used to remove Sb with high removal rates reported (85-99%) (Guo et al. 2009).

Table 7.4 Summary of technologies capable of removing Hg and Sb to concentrations below UK (Hg 0.05 µg/L, Sb 5 µg/L) and US (Hg 0.77 µg/L, Sb 5.6 µg/L) standards.

Technology Classification	Treatment Outline	Advantages	Limitations	Factors Influencing Removal
<i>Adsorption</i> Synthetic Adsorbent Biosorbents	Adsorption involves adhesion of ions, atoms or molecules from dissolved solid, liquid or gaseous phases to a surface (Stumm and Morgan, 2012). Adsorption can be reversible, allowing adsorbent regeneration through desorption processes (Fu and Wang, 2011).	Cost-effective, design flexibility, produces high quality effluent	Contaminant sensitivity-fouling and plugging, spent media disposal	Contaminant concentration, pH, flow rate, fouling, spent media
<i>Bioremediation</i> Bioreactors	Bioreactors are vessels in which chemical processes occur, involving organisms directly or organism-derived biochemically active substances. A supply of chemically inert free-flowing medium, which acts as a receptacle, allows bacterial breakdown of sewage. This mechanism can be aerobic or anaerobic (Grady Jr et al. 2012).	Continuous operation, temperature control, simple construction	Pre-treatment requirements, solids disposal	pH, temperature, available nutrients, contaminant concentration
<i>Chemical</i> Precipitation Coagulation/ flocculation	Precipitation involves chemical reactions with heavy metal ions forming insoluble precipitates, which are extracted from water using sedimentation and filtration techniques (Fu and Wang 2011). Coagulation involves wastewater charge neutralisation and the formation of a mass which is a sufficient size to be trapped through filtration (Mazille 2015). Flocculation defines the stirring/agitation procedure applied to encourage particle agglomeration (Mazille 2015).	Simple operation, low capital cost	Sludge generation, sludge disposal cost	Other compound presence, pH, chemical dosage, sludge disposal
<i>Membrane Filtration</i> Ultrafiltration (UF) Reverse Osmosis (RO) Nanofiltration (NF)	UF works at low transmembrane pressures for the removal of colloidal and dissolved material (Ersahin et al. 2012). RO uses a semi-permeable membrane, which allows fluid being purified to go through, while rejecting contaminants. RO has high pumping pressures and requires the restoration of membranes. NF is an intermediate process between RO and UF, in which benefits occur from ease of operation and reliability, whilst comparatively low energy consumption and greater efficiency are also achieved (Ersahin et al. 2012).	High separation selectivity, small space requirement	Membrane fouling, high energy/operational cost	Contaminant concentration, molecular weight of contaminants/solids, characteristics of untreated water
<i>Ion Exchange</i>	Ion-exchange resins, whether they are naturally solid or synthetic, instigate cation exchange with metals in wastewater. Synthetic resins are predominantly used due to their reported higher efficiency, whilst commonly used cation exchangers are strongly acidic resins with sulfonic acid groups or weak acid resins with carboxylic acid groups (Gode and Pehlivan 2006).	Low time consumption, no sludge generation	High capital cost, only some resins suitable for metal removal	pH, temperature, contact time, initial metal concentration, ionic charge

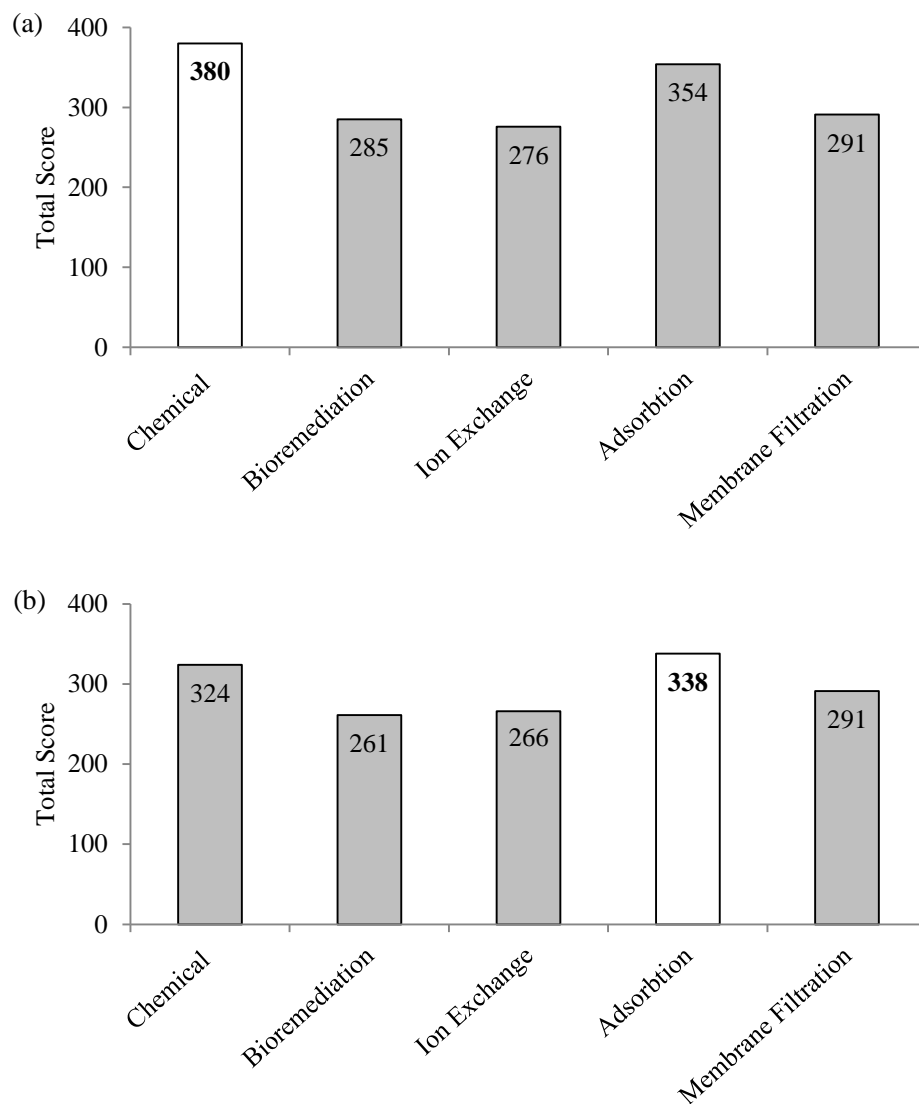


Figure 7.5 Results of Kepner Tregoe analysis on technologies for the removal of Hg (a) or Sb (b) from effluent streams at the works.

7.4 Discussion

7.4.1 Mercury and antimony occurrence throughout wastewater treatment

Mean Hg concentrations in influent at the works ($0.09 \mu\text{g/L}$) are higher than the average value ($0.07 \mu\text{g/L}$) recorded for 16 WWTWs throughout the UK (Gardner et al. 2013). The value for the works is however less than mean influent concentrations ($0.5 \mu\text{g/L}$) observed by Rule et al. (2006) for UK WWTWs, whilst large industrial inputs have led to values as high as $1.6 \mu\text{g/L}$ observed in influent (Lester, 1987). From a global perspective Ribeirao Preto WWTWs (Brazil) serves over 1000 diverse industrial

activities and although the majority of these are defined as small businesses (chemical, medical and food industries) many contribute to the 0.1 µg/L Hg concentration observed in influent samples (da Silva Oliveira et al. 2007). A mean influent Hg concentration of 0.1 µg/L was also recorded at Henriksdal WWTWs (Sweden) with dental inputs recognised as having a prominent contribution (Sörme and Lagerkvist, 2002). Dental wastes, more specifically amalgam, were previously found to be responsible for 53% of global Hg emissions (World Health Organization [WHO], 2013), with up to a 50% contribution to influent concentrations observed at WWTWs (Bender, 2008). However Hg has been subject to source control with the Minamata Convention treaty, agreed by the United Nations Environment Programme (UNEP) in 2013, stating that progress must be made to reduce the use of Hg in dentistry, encouraging use of non-mercury containing alternatives (UNEP, 2013). Consequently high influent concentrations of Hg at WWTWs in the present day often refer to wastewater infiltrated with landfill leachate and/or agricultural chemicals such as fertilisers (Wang et al. 2004). From a locational perspective the site studied is not in the vicinity of landfill or agricultural operations, predominantly receiving industrial influent. It is therefore suggested that relatively low influent concentrations of Hg at the works, compared with findings by Rule et al. (2006), has resulted from dentistry practice changes, reflecting expected findings for global WWTWs (Mackey et al. 2014).

The relatively high mean influent Hg concentration (0.09 µg/L) observed at the works in comparison to post Minamata Convention values at WWTWs in the UK (0.07 µg/L; Gardner et al. 2013) was not suggested to be unusual, as the value recorded was still within the range reported in the Chemicals Investigation Programme (CIP) (Gardner et al. 2013). However high influent concentrations of Sb compared with typical concentrations (0.2 µg/L - 0.4 µg/L) outlined by Choubert et al. (2011) were associated with the high industrial inputs at the works. These inputs contain high Sb concentrations amid contributions from consumer electronics and paints which have ever-increasing obsolete characteristics (van Velzen et al. 1998).

7.4.2 Mercury fate and removal throughout wastewater treatment

Hg fate and removal throughout the wastewater treatment process is influenced by interactions of this metal with TSS and organic compounds (Vernon and Bonzongo,

2014). Hg has a strong association with both these components and this relates to high sorption characteristics of this metal (McKay et al. 1989). This attribute is demonstrated using the metal partition coefficient (K_d), which is the ratio of sorbed metal concentration to dissolved metal concentration at equilibrium (Allison and Allison, 2005). For Hg, surface water studies have found relatively high K_d values for partitioning with suspended solids (4.7) and dissolved organic carbon (DOC) (5.4), demonstrating that mercury portrays high affinity for both organic and inorganic particulate matter (Allison and Allison, 2005; Bravo et al. 2011). Although studies which have calculated K_d values for Hg in wastewater are limited, Hg has been found to demonstrate high affinity for TSS and organic compounds within WWTWs (Goldstone et al. 1990; Wagner-Döbler et al. 2000). This is reflected at the site studied with significant positive correlations found between Hg and TSS removal as well as Hg and COD removal. Removal of Hg within primary treatment at the site is relatively low (53%) compared with the global average (62%) recorded by Ziolkowski et al. (2011), however shows a similar removal rate to findings in Canada (54%; Oliver and Cosgrove, 1974) and in the US (57%; Barth et al. 1965). This suggests that primary treatment has satisfactory Hg removal at the works, but removal increases are achievable through operational solutions such as lengthening HRT (Petrie et al. 2014).

Reduced Hg removal within secondary treatment (30%) compared with primary treatment (52%) at the works (Figure 7.2) is expected and is suggested to result from metal accumulation onto biosolids, due to the recirculation of returned activated sludge (RAS) (Figure 7.1). This process enhances metal content per mass of solids and subsequently concentrations found in effluent (Huang and Wang, 2001). Chen et al. (1974) determined that within biological treatment 45-55% of Hg present was associated with settleable particulates, subsequently stating that Hg is removed by adsorption onto bacterial solids. Physico-chemical adsorption of soluble Hg to AS has also been documented (Wu and Hilger, 1985) with Hg complexes (with organic compounds) adsorbing onto the surface of suspended solids or microbiological communities (Guo et al. 2009). This is reflected within the significant positive correlation found between Hg and TSS removal at the works.

Secondary treatment Hg removal at the works (30%) was lower than the global average for biological treatment at AS works (68%) (Ziolko et al. 2011), whilst UK AS works, such as Whitlingham WWTWs (Norwich, England), demonstrated mean removal of 47% (Goldstone et al. 1990). Within secondary treatment at the works a lower rate of removal for Hg compared with primary treatment coincided with TSS and COD removal increases (Table 7.2). These findings are reflected within a works studied by Goldstone et al. (1990), who found this resulted from high Hg concentrations entering the treatment process from returned sludge liquors. Sludge returns prevent dissolved Hg from attaching to the surface of particles, therefore enhancing final effluent metal concentrations (Goldstone et al. 1990). This is suggested to reason why a lower rate of removal was recorded for secondary treatment at the works studied. More specifically cake pad run-off is suggested to be the prominent influence as this return has consistently higher mean Hg concentrations compared with other sludge sampling locations throughout all seasons studied (Figure 7.3b). Furthermore, as the flow sheet suggests (Figure 7.1), this return is not accounted for within the influent samples collected and analysed at the site.

Despite specific sludge return attribution it must be considered, however, that all sludge samples contained Hg (Figure 7.3b) with wide ranging concentrations observed for all locations at the works (Figure 7.3b). These inputs can inhibit site operations by reducing sludge settleability, however this has not occurred at the site with a satisfactory primary tank performance observed (Table 7.2). Nevertheless increasing Hg concentrations within the works, which all sludge returns contribute to, reduces metal removal elevating final effluent concentrations, with a correlation existing between increasing metal concentration and decreasing metal removal (Chipasa, 2003).

7.4.3 Antimony fate and removal throughout wastewater treatment

Due to the typical low abundance of Sb in wastewater (0.2 -0.4 ug/L) (Choubert et al. 2011), Sb wastewater studies have been largely neglected to date and therefore there is a lack of existing data on Sb partitioning in WWTWs. However, published data on Sb partition between solid and dissolved phases in surface waters clearly indicates that Sb is almost exclusively present in the dissolved phase (Jarvie et al. 2000; Filella et al. 2002) with K_d values as low as 2.7 reported for Sb in surface waters (Allison and

Allison, 2005). Tanizaki et al. (1992) also reported that in river water 90% Sb was in the soluble phase ($<0.45\ \mu\text{m}$) with further fractionation analysis of this phase identifying that 70% of soluble Sb was associated with materials $< 500\ \text{Da}$ in diameter. Although it is recognised that surface waters contain different particulate species to those found in wastewater the pH range (pH 7-9) is equivalent therefore Sb is anticipated to have a high solubility in wastewater regardless of its oxidation state (Filella et al. 2002). Weak interactions between Sb and suspended particles are anticipated to exist in wastewater (Filella et al. 2002) and this is supported by the significant negative correlation observed between Sb and TSS removal at the studied works and the low removal rate (16%) observed for Sb throughout primary treatment at the works.

Thermodynamic analysis attests that Sb exists as Sb(V) in oxic and Sb(III) in anoxic environments (Filella et al. 2002) and, despite limited systematic studies existing on this aspect, it has been determined that Sb within wastewater treatment is unstable (Han-Wen et al. 1982). Instability is prominent within the AS process amid fluctuating anaerobic and anoxic conditions (Figure 7.1). The high solubility and instability characteristics of metals, such as Sb, are correlated with low, if any, removal throughout AS treatment (Brown et al. 1973). This relates to the low complexation capacity of these metals and subsequently a low affinity for AS biomass (Lester, 1983). Whilst the availability of metals, such as lead (Pb), which readily form stable, insoluble complexes with sewage sludges (Brown et al. 1973) is also a contributing factor to low removal. Accounting for these characteristics it can be suggested that any complexes formed between extracellular polymers and Sb will be weak, as such during AS treatment oxidation of polymers is likely to result in Sb release back into effluent. This phenomenon has been observed for cadmium (Cd) and arsenic (As) (Lawson et al. 1984) and is subsequently suggested to contribute to the negative Sb removal (-29%) existing within secondary treatment at the works. However further examination of Sb speciation within wastewater is required to confirm this suggestion.

Increases within Sb concentrations across the works (Table 7.2), reflected within the overall calculated removal (-15%), was suggested to result from Sb being imported with sludge to the works. Sb within imports was suggested to predominantly exist within the free ionic form, demonstrating a low sorption potential and little affinity for suspended

solids (Fillela et al. 2002). This finding was reflected within the significant negative correlation between Sb and TSS removal at the works. Returned sludge liquors, which demonstrated wide ranging Sb concentrations for all sludge sample locations (Figure 7.4b), were therefore suggested to contribute to the variable and elevated final effluent concentrations at the site (Table 7.2).

7.4.4 Operational solutions to enhance mercury and antimony removal

Most effective operational solutions to enhance metal removal during primary settlement relate to lengthening HRT, with metal concentrations found in settled sewage reduced with increasing HRT (Petrie et al. 2014). This results from high proportions of metals, including Hg, in influent being associated with particulates (Wang et al. 2014). Enhancements to HRT in most instances, including at the site studied, would require infrastructural developments as sufficient space is not present with onsite storm tanks and remote holding tanks are unavailable to act as counter-balances for fluctuating sludge flows (Petrie et al. 2014). In addition, enhanced HRT requires improved primary treatment through enhanced particulate bound metal removal to prevent solubilisation within secondary treatment (Kumar et al. 2014). An alternative to increasing primary settlement tank sizes involves the use of micro-screens which are determined to improve TSS removal with a comparatively reduced footprint (Unger and Brinker, 2013).

Metal removal within biological (secondary) treatment that incorporates AS matrices relies entirely on partitioning (Ziolko et al. 2011). This is dictated by three processes; physical entrapment of insoluble metals, binding of soluble metals to extracellular polymers/bacterial walls and active cellular uptake by bacterial cells (Ziolko et al. 2011). Partitioning is the main removal pathway for metals amid increased concentrations observed in the particulate phase of RAS at each sludge retention time (SRT) increase (Petrie et al. 2014). Total metal removal is therefore correlated with enhanced SRT amid AS comprising of smaller flocs, increasing floc surface area and subsequently binding site availability (Stoveland and Lester, 1980; Petrie et al. 2014). Enhancing SRT instigates decreases in effluent SS and COD, whilst increasing sludge volume (Stoveland and Lester, 1980). Consistent SRT is therefore desired at works to develop better process control and continuity. This can be achieved operationally by using in situ SS probes and real-time flow measurements. It must be considered that

increased SRT is correlated with greater aeration demands and subsequently costs (Amanatidou et al. 2015). Although it has been shown by Leu et al. (2012) that higher SRT achieves improved oxygen transfer due to smaller and more uniform AS flocs, it has been found that Hg concentrations are unaffected by SRT (Conklin et al. 2007).

Significant variations within sewage flows at the works (16488 - 96274 m³/d) results in a dynamic system that experiences significant variation within SRT and HRT (Petrie et al. 2014). The inability to feasibly enhance HRT and increasing costs associated with lengthened SRT means that operational solutions are not sustainable options for Hg and Sb management at the site studied. Consequently metal removal technologies need to be considered for additional treatment.

7.4.5 Technologies for sludge liquor treatment

Heavy metals, such as Hg, in sludge liquors are suggested to adhere to microorganism cell surfaces (Yoshizaki and Tomida, 2000). Therefore, enabling potential technology implementations to remove metals existing on these surfaces (Volesky, 1990).

Biopolymers existing within sludge have low affinity characteristics, emitting buffer action toward inorganic acids (Yoshizaki and Tomida, 2000), rendering them ineffective for Hg removal. However, research conducted on diverse acid types determined that phosphoric acid (H₃PO₄; 43%) instigates efficient Hg removal (100%) (Yoshizaki and Tomida, 2000) on a laboratory scale. H₃PO₄ demonstrates high affinity for biopolymers therefore can easily make contact with metals that exist in the vicinity, effectively dissolving them. In addition, heavy metals in H₃PO₄ solutions (after extraction) are removed with ease by cation-exchange resin processing (Yoshizaki and Tomida, 2000). It must be considered that use of H₃PO₄ of this concentration (43%) would exhibit unsustainable chemical usage and financial costs. Reduced concentrations lead to reduced removal rates with H₃PO₄ (8.5%) demonstrating 46% removal (Yoshizaki and Tomida, 2000). This trend supports the findings of Stylianou et al. (2007) who state that removal rates for precipitation are enhanced following increases in acid concentration, temperature and contact time. Inflation of these parameters results in an enhancement of the offered energy for the breakdown of chemical bonds of metals found in sludge (Stylianou et al. 2007).

It is acknowledged that biosorbents can remove metals from sludge by ion exchange and adsorption (Hu et al. 2015). Both these mechanisms are influenced by biosorbent components and operational conditions with lengthened HRT and SRT enhancing technique removal rate (Stoveland and Lester, 1980; Petrie et al. 2014). Ion exchange removal of heavy metals from sewage sludge is however suggested to yield relatively low efficacy (50-60%), with both gel and macroporous cation exchange resins demonstrating similar effects (de Villiers et al. 1995). Adsorption mechanisms, applied to sewage sludge, are influenced by TSS and organic compounds which in most instances cause media fouling and plugging, therefore requiring pre-treatment with flocculation, settling and filtration or oil-water separation (Hu et al. 2015). These limitations alongside the influence of colloids are also responsible for membrane fouling (Fu and Wang, 2011). Membrane filtration is therefore suggested to be unfeasible for sludge treatment amid excessive costs and maintenance requirements. Despite adsorption limitations alkali adsorption treatment has been deployed. Alkali treatment is a biosorbent method to enhance sewage sludge adsorption capacity, increasing complexation through the formation of more ionized functional groups (Hu et al. 2015). This technique indicates the following bonding affinity trend for alkali treated sewage sludge to heavy metals $Pb > Cd > Nickel (Ni)$ (Hu et al. 2015), demonstrating that alkali treatment may effectively remove Hg as this element shows similar binding affinity to Pb (Bailey et al. 1999).

There are currently no studies available which demonstrate the application of technologies to remove Sb from sludge streams at WWTWs. This is suggested to relate to the presence of Sb in anionic form and its characteristics, which include low binding affinity with TSS, organic compounds or microorganisms (Fillela et al. 2002). Therefore despite technologies being available for the removal of metals from sludge liquors they are not currently commercially available at full scale, therefore current effluent treatment technologies should be considered.

7.4.6 Technology selection: additional treatment of effluent stream

Bioremediation has a relatively high footprint and to achieve desired concentrations for both Hg and Sb the implementation of buffering tanks are required for wastewater dilution to enable continuous works operation (Wagner-Döbler et al. 2000). To achieve

effective rates of removal an activated carbon filter should also be used in combination (Wagner-Döbler et al. 2000). Despite relatively low chemical usage and maintenance requirements bioremediation is foreseen to be an unsustainable option, particularly considering this technology is seldom implemented for Hg and Sb removal (Mani and Kumar, 2014). This characteristic is also apparent for ion exchange. Ritter and Bibler (1992) state that Duolite™ GT-73 resin demonstrates reliable removal of Hg and suggest this resin would effectively remove Sb. Relative uncertainty within the removal ability of synthetic ion exchange resins from effluent, which also include sulfonated polystyrene-divinylbenzene and Amberlite 252 (Monteagudo and Ortiz, 2000), has however led to the development of alternative solutions (Wang and Peng, 2010). Natural zeolites (naturally occurring silicate minerals) are used for metal removal due to their high abundance and relatively low costs (Karman et al. 2015). Though reported usage of zeolites is becoming more frequented they are limited at present compared to synthetic resins and are predominantly implemented at laboratory scale (Gode and Pehlivan, 2006; Karman et al. 2015). This alongside the observation that ion-exchange resins are implicated by initial metal concentrations (Gode and Pehlivan, 2006), which for Hg and Sb are low ($\mu\text{g/L}$ ranges), sufficiently decreases potential removal rates achieved (Barakat, 2011). Therefore reasoning why low total KT scores were attributed to this technology for both Hg (276) and Sb (266) removal (Figure 7.5a and b, respectively).

Membrane filtration has demonstrated effective removal of Hg from wastewater effluent (Uludag et al. 1997; Chiarle et al. 2000) and effective Sb removal, to provide drinking water/high purity water with Sb concentrations in $\mu\text{g/L}$ ranges (Kang et al. 2000). This technology also demonstrates space saving and easy operation characteristics (Fu and Wang 2011), however displays low total values within KT analyses (Figure 7.5a and b) due to its unsustainable nature. Membrane filtration demonstrates high CAPEX and maintenance requirements (from membrane fouling) (Kang et al. 2000; Fu and Wang, 2011) as well as high energy needs, such as adsorption pre-treatment to instigate Hg formation as precipitates. These requirements are necessary to maintain stable operations and obtain higher flux rates which equate to high carbon and financial costs (Wiesner et al. 1994; Fu and Wang, 2011).

Adsorption has been deployed for Hg removal with granular activated carbon (GAC) acknowledged to be effective, amid Hg complexes with organic compounds readily adsorbing onto the surface of TSS or microbiological communities (Guo et al. 2009). However regeneration of GAC involves heating to desorb contaminants which release volatile Hg compounds. Further treatment is also necessary before spent media can be disposed making large scale application expensive (Sharma et al. 2014). Adsorption techniques therefore demonstrate high maintenance requirements (spent media disposal), high chemical usage and high CAPEX costs (to implement further treatment). These factors reason why adsorption has a lower total KT score (354) than chemical techniques (380) for Hg removal (Figure 7.5a). Chemical techniques, however, have a lower total score for Sb compared with Hg removal and this is because despite chemical mechanisms being commonly used they are not specifically designed for Sb removal and therefore exhibit low removal efficiencies (Kang et al. 2003). Guo et al. (2009) did however report 98% removal of Sb after conducting pH adjustments and dosing with ferric coagulants, which are found to be more effective than alum and lime coagulation (Ungureanu et al. 2015). Precipitation may occur but Sb would have to compete with other compounds found within effluent for sulphates and indeed metals (Guo et al. 2009).

7.4.6.1 Final selection: additional treatment to enhance mercury and antimony removal

Chemical techniques are most commonly used metal removal technologies within effluent streams (Fu and Wang, 2011). They are a low cost option that can treat large volumes of wastewater (Karman et al. 2015). More specifically sulfide precipitation is found to accomplish outflow Hg concentrations $< 1 \mu\text{g/L}$ without issue, amid the ability of Hg to readily react with sulphide forming mercury sulphide (HgS) (Guo et al. 2009). However handling of the toxic HgS produced requires extensive safety measures and chemical usage (Wagner-Döbler et al. 2000). This limitation is however offset by the ability of chemical techniques to be effective over a wide pH range and exhibit operation simplicity (Ungureanu et al. 2015). These factors demonstrate why the highest total KT score for Hg was attributed to chemical techniques (Figure 7.5a). Large metal inputs at the head of the works, particularly from cake pad run-off and sludge belt

returns (Figure 7.3b), means that for Hg removal chemical treatments to influent (including site returns) before it enters primary treatment is the most suitable option. This implementation would raise system pH and precipitate dissolved metals as hydroxides, which would settle out in primary settling tanks before secondary treatment commences (Oliver and Cosgrove, 1974). This is suggested to be a distinct advantage of precipitation as deployment of adsorption and ion exchange would be most appropriate after primary treatment to prevent equipment clogging and prohibit metals from reaching micro-organisms (Oliver and Cosgrove, 1974).

The highest KT value for Sb removal was adsorption (338). A variety of adsorbents have been used to remove Sb, it has been reported that adsorption is most effective with Mn, Fe and Al ligands (Belzile et al. 2001) with high removal rates achieved (85-99%) as Sb has no preference to bind with organic compounds (Guo et al. 2009). Adsorption is therefore most suitable for Sb removal from effluent streams at WWTWs (Ungureanu et al. 2015). More specifically, at the site studied, granulated ferric hydroxide (GEH) is suggested for implementation. This is a relatively new adsorbate, developed at the Department of Water Quality Monitoring (Berlin University), and has been shown to effectively remove Sb to levels below 5 µg/L (Ilavský, 2008).

7.5 Conclusions

- Fate and removal of Hg at the works was influenced by the positive correlations observed between this metal and TSS as well as COD removal rates. This association results from the high sorption characteristics of this metal.
- Sb had a weak interaction with suspended particles in wastewater treatment and was therefore not affected by TSS removal at the works.
- Elevated final effluent Sb concentrations compared with influent values was suggested to result from Sb being imported with sludge to the works. Returned sludge liquors are therefore suggested to be responsible for variable and elevated final effluent Sb concentrations at the works. Sludge returns are also suggested to increase Hg concentrations within the works, reducing Hg removal and increasing final effluent Hg concentrations.

- Operational solutions, specifically enhanced HRT and SRT, are an option to increase Hg and Sb removal but are not applicable for implementation at the works studied due to limited capacity for expansion and high costs of infrastructural development. Whilst treatment technologies deployed on sludge liquors require further development before they can be implemented commercially.
- A variety of technologies are available for additional treatment at the works to remove Hg and Sb to levels below UK (Hg: 0.05 µg/L; Sb: 5 µg/L) and US (Hg: 0.77 µg/L; Sb: 5.6 µg/L) standards. It was determined that chemical techniques, more specifically precipitation, were most suitable for Hg removal. Whilst adsorption was selected as most appropriate for Sb removal, in particular the use of the adsorbate GEH.

7.6 References

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Chapter 8

Conclusions

8. Conclusions

The conclusions of this research in relation to the original objectives are as follows:

Objective 1: Review the current knowledge on the fate and removal of metals during conventional wastewater treatment processes and the effectiveness of existing advanced treatment types.

- The form of a metal is the critical factor influencing fate and removal within the wastewater treatment process. Previous work in this area, however, limits the distinction of metals to particulate ($> 0.45 \mu\text{m}$) and soluble ($< 0.45 \mu\text{m}$) size fractions. This distinction is simplistic since the soluble fraction contains both colloidal and dissolved materials to which metals can be associated, and may thus impact on design of wastewater treatment processes (Chapter 2).
- A review of the current design and practice at municipal wastewater treatment works (WWTWs) found that removal rates in both primary and biological treatment stages are inconsistent, regardless of the applied treatment type (i.e activated sludge or trickling filters). Consistent and stable rates of removal are difficult to achieve (Chapter 2).
- Operational parameters, such as retention time, affect removal rates and may be optimised to enhance metal removal, but increase the cost of treatment, require space, and their removal performance is inconsistent. Therefore, to consistently reduce concentrations of metals in wastewater the application of advanced treatments may be preferred (Chapters 2, 7).
- When reviewing advanced treatment technologies, it was found that previous research has focused on the study and application of energy/carbon intensive and expensive treatment processes that, in most instances, are unsuitable for widespread application. Therefore, the development of a low cost treatment technology that can effectively remove metals at municipal wastewater concentrations is required, to allow WWTWs operators to better control metal concentrations in effluent discharges (Chapter 2).

Objective 2: Evaluate the distribution of Cu, Pb, Ni and Zn in particle size fractions of wastewater.

- The distinction of colloidal and truly dissolved fractions within the soluble phase is essential to understand the potential options to enhance the removal of metals from wastewater. In effluent, a substantial proportion of Cu, Pb, Ni and Zn was associated with colloidal material within the colloidal size fraction. This shows that techniques capable of eliminating materials from the colloidal fraction could reduce the concentration of these metals in effluent discharges (Chapters 3, 5).

Objective 3: Investigate the coagulation-flocculation (CF) process for the removal of trace metals from municipal wastewater, and evaluate the impact of this treatment process on metal form (i.e. particulate, colloidal, and truly dissolved fractions), bioavailability and removal.

- The CF process using either the metal salt ferric chloride (FeCl_3) or the biopolymer Flocculan are effective at removing Cu, Pb and Zn from effluent at concentrations typically found in municipal wastewater. CF therefore presents an opportunity to mitigate compliance risk that may otherwise be attempted by the application of technologies with much greater cost and energy consumption implications (Chapters 4, 5).
- Neither FeCl_3 or Flocculan were able to remove Ni. Indeed, the metal salt FeCl_3 was found to increase the concentration of Ni in effluent as a consequence of its occurrence as an impurity in FeCl_3 . The consistent removal of Ni from municipal wastewater remains a significant challenge (Chapters 4, 5).
- The dominant mechanism for particle removal by FeCl_3 was enmeshment in a growing hydroxide precipitate, known as sweep flocculation. Whereas, Flocculan is composed of positively charged polymeric chains that neutralise particles; this enables aggregation and removal through the mechanism of inter-particle bridging. Thus, reagents used in the CF process are unique with regards to the removal mechanisms involved (Chapters 4, 5).

- Metals distributed in the particulate and colloidal size fractions of effluent can be removed using CF, but metal in the truly dissolved fraction cannot typically be removed. Flocculant, however, reduced the concentration of Cu in the truly dissolved fraction, revealing an additional point of removal. Hence, insight into the relationship between metal fractionation and CF was essential for diagnosing their removal pathways (Chapter 5).
- The concentration of dissolved organic carbon (DOC) in effluent is a crucial parameter influencing metal bioavailability. Whereas Flocculant and FeCl_3 offer similar removal rates for the studied metals (except for Cu, for which flocculant is better), Flocculant does not reduce the DOC concentration and therefore simultaneously reduces the concentration of metals and their bioavailability in treated effluent. FeCl_3 was found to offer a broadly proportional reduction in metal and DOC concentration (neutral impact on bioavailability) therefore offering limited environmental benefit (Chapter 5).

Develop an improved understanding of the factors that influence the fate and removal of mercury (Hg) and antimony (Sb) throughout the wastewater treatment process at a specific WWTWs, and examine the technology options available to improve removal.

- Hg was predominantly associated with particulate materials owing to strong correlation with total suspended solids (TSS), therefore chemical precipitation (with sulphuric acid) was identified as the most suitable treatment option. Conversely, Sb had a weak interaction with suspended particles and was therefore not affected by TSS removal. Thus, a more expensive and energy intensive process would be required for the effective removal of Sb; adsorption using granulated ferric hydroxide was identified to be most appropriate (Chapter 7).

Appendices

Appendix A Structural characteristics of ferric chloride

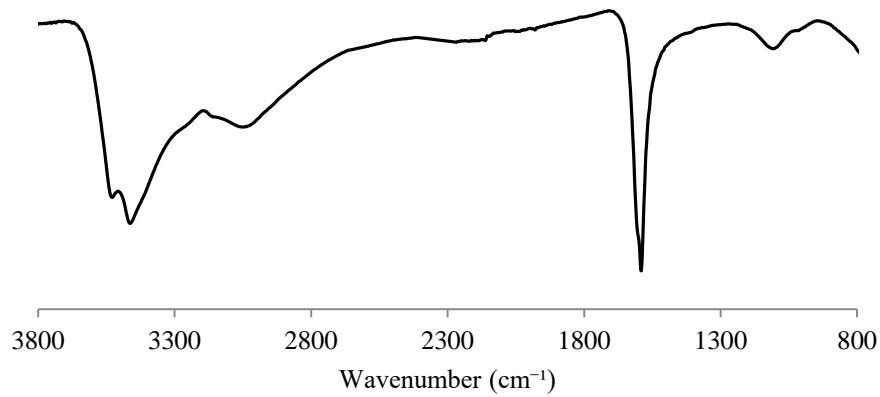


Figure A.1 FTIR spectrum for ferric chloride (FeCl_3) (0.81 FDM library match score).

Appendix B Estimated treatment costs for Flocculant and ferric chloride

Table B.1 Estimated treatment costs for Flocculant and FeCl_3 .

Coagulant	Price (£/mg)	Quantity (mg/L)***	Treatment Cost (£/L)****	Cost Ratio*****
FeCl_3	0.0000016*	0.10	0.00000016	1 : 10
Flocculant	0.0000065**	0.25	0.000001625	

* A. Major (2017), personal communication

** A. Lee (2017), personal communication

*** Established optimum dosage (Chapter 5)

**** Price multiplied by quantity

***** Flocculant treatment cost / FeCl_3 treatment cost